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Sulfide Treatment of Acid Mine Drainage

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Sulfide Treatment of Acid Mine Drainage

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

DEPARTMENT OF THE INTERIOR

by

Bituminous Coal Research, Inc.
350 Hochberg Road
Monroeville, Pennsylvania 15146

Program Number
FWPCA Grant No. 14010 DIJ

November, 1969

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ABSTRACT

The studies reported herein were a continuation of a 12-month program initiated in June 1967 with funds from the Appalachian Regional Commission. During this earlier program a process for the treatment of coal mine drainage was conceived, involving the combined addition of limestone and hydrogen sulfide to effect precipitation of iron sulfides (LHS process).

Results of laboratory-scale continuous flow tests of the LHS process during the current program indicated that hydrogen sulfide feed must be accurately predetermined and controlled to effectively precipitate iron, yet to avoid an excess of reagent in the process effluent.

The black sludge formed during treatment undergoes oxidation at a rate depending on drying conditions, with formation of elemental sulfur. X-ray diffraction analyses indicate the iron sulfide sludge component is an amorphous material, although chemical analyses indicate it is initially a stoichiometric compound whose empirical formula corresponds to that of ferrous sulfide.

The unstable nature of the sulfide sludge, possibility of polysulfide formation during treatment, instability of mine waters of the type amenable to treatment, and inadequacies of available gas metering equipment are among the factors which militate against the controlled regulation of hydrogen sulfide feed necessary for successful operation of the process. These factors, and additional disadvantages revealed by an updated cost evaluation, lead to the conclusion that the LHS process is less attractive than accepted methods of mine drainage treatment.

The current program was cosponsored by the Federal Water Pollution Control Administration (FWPCA) and the coal industry through its research agency, Bituminous Coal Research, Inc.

This report was submitted in fulfillment of project (FWPCA Grant No. 18010 DIJ) between the Federal Water Pollution Control Administration and Bituminous Coal Research, Inc.

Key Words

Coal Mine Drainage
Iron Sulfides
Pollution Abatement
Limestone
Hydrogen Sulfide
Sulfides
Waste Water Treatment
Stream Pollution

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Attempts to promote crystal ordering of the iron sulfide specie(s) in the sludge through heating to moderately elevated temperatures (e.g., 100 C) under vacuum.

Further study of factors affecting the hydrogen sulfide stoichiometric requirement, with particular attention to the formation and stability of polysulfide species.

Further tests, supplemented by zeta potential measurements, on the use of cationic coagulant aids to promote sludge settling, for the purpose of determining optimum dosages, methods of application, and relative effectiveness.

Verification of the exact hydrogen sulfide stoichiometric requirement for quantitative precipitation of iron during treatment through the use of pure ferrous sulfate and ferric sulfate solutions, and mixtures thereof.

In terms of the longer-range goals involving adaptation of the IJH process for the continuous treatment of mine drainage, further consideration should be given to:

The volume of mine water available for treatment with a high ferrous:ferric iron molar ratio, relative to the total volume of coal mine drainage.

The development of more rapid and more accurate methods for the determination and control of hydrogen sulfide feed during treatment. This could involve work in such areas as the development of more rapid analytical techniques for ferrous and ferric iron, automatic measurement and control of hydrogen sulfide in the process effluent, and the development of more reliable gas metering equipment.

The possible effects of changing chemical composition and physical properties of the sludge after treatment, as they pertain to the feasibility of a reagent recovery step in the process.

The actual economic feasibility of a reagent recovery-recycle step in the overall process.

Section 1

CONCLUSIONS & RECOMMENDATIONS

Conclusions

The following conclusions appear to be supported by the results presented herein:

Regarding the process wherein limestone and hydrogen sulfide are used in combination for the treatment of coal mine water (LHH process), experience has indicated that the technique of utilizing a closed vessel in which limestone, hydrogen sulfide, and mine water are intimately mixed, is the most feasible method for achieving the desired precipitation of iron.

Hydrous ferric oxide, previously precipitated by natural oxidation or limestone neutralization of mine water, is rapidly reduced in suspension near pH 6 by hydrogen sulfide. Elemental sulfur is a byproduct of this reduction reaction. Consequently, hydrogen sulfide feed calculations should be based on concentrations of both ferrous and ferric iron rather than on ferrous iron concentration alone.

In the absence of sufficient hydrogen sulfide to precipitate all iron as the sulfide, ferrous iron formed by hydrogen sulfide reduction of ferric iron may be in equilibrium with hydroxyl ion and ferrous hydroxide. This may account for the apparent resolubilization of ferrous iron from the sulfide sludge observed during some experiments.

Accurate determination of the hydrogen sulfide feed requirement is necessary for the successful operation of the LHH process in terms of the amount of iron removed. Such accurate determination was found to be difficult because of the occurrence of iron oxidation during the brief storage of mine water samples collected for continuous flow treatment experiments.

Results of a refined analytical technique for sulfide sulfur and iron indicate that the iron sulfide species in the freshly formed sludge is a stoichiometric compound corresponding to the empirical formula FeS.

The sulfide component of the sludge itself (presumably ferrous sulfide initially) is unstable with respect to oxidation, and undergoes decomposition in suspension or on exposure to air with the formation of elemental sulfur and, probably, amorphous ferric oxyhydroxide. If dried rapidly at room temperature by acetone washing and pulverized to a fine powder, or if dried in air in an

oven held at 110 C, the sludge undergoes a strongly exothermic reaction which is probably the result of rapid oxidation.

The ease of oxidation of the sludge, and the absence of lines corresponding to those of known iron sulfide compounds in x-ray diffraction patterns of freshly formed sludge samples, indicate that the iron sulfide component of the sludge formed under the prevailing experimental conditions is an amorphous, structurally disordered, and (presumably) hydrated material. The sulfide sludge can apparently be preserved temporarily in its original state by vacuum drying at room temperature.

The elemental sulfur (probably of colloidal size) formed during sludge oxidation or ferric iron reduction may undergo reaction with the hydrosulfide ion (HS^-) with the formation of soluble polysulfide species. This may result in a significant loss of hydrogen sulfide in the system, in terms of its availability for reaction with iron.

Freshly precipitated suspended sludge particles from the LHH treatment process are negatively charged. Cationic flocculating aids are effective in promoting coagulation and more rapid settling of the LHH sludge; anionic flocculating aids, used alone, are not effective in this regard.

The sludge obtained from LHH treatment of one mine water, after gravity settling, had a smaller volume and a higher solids content by weight than sludges obtained by either lime or limestone treatment of the same mine water.

A current evaluation of the LHH process in terms of its technological soundness and economic feasibility indicates that the process is less attractive than accepted methods of treatment relative to its applicability to different types of mine waters, its ease of control, its simplicity in implementation, and its costs of operation.

Recommendations

It is felt that future efforts should include activities in the following areas:

Additional studies of ferric iron-hydrogen sulfide reactions with the use of varying amounts of hydrogen sulfide; identification of the solid reaction products, and determination of changes in the oxidation states of iron species (both soluble and insoluble) with time.

Investigation of material balances for sulfur in the sludge, in an effort to determine the extent of sulfur formation during oxidation of the iron sulfide component of the sludge.

Section 2

INTRODUCTION

Water pumped from active coal mines and water draining from abandoned coal mines are both potential sources of water pollution. The composition of such mine water can generally be described as a mixture of metallic sulfates in an acidic or alkaline solution together with a varying amount of suspended solids. Of primary importance in establishing the degree of pollution of any mine discharge is the concentration of dissolved iron and, to a lesser degree, the concentrations of aluminum and manganese. The discharge of untreated mine water into the stream can lead to the pollution of the receiving stream water. Dilution of the mine discharge by the receiving stream generally causes an increase in pH which subsequently causes hydrolysis of the ferric iron present; this in turn provides an environment conducive to rapid ferrous iron oxidation which then leads again to hydrolysis and precipitation of the hydrous iron oxides familiarly known as yellowboy.

To eliminate the source of pollution from coal mine discharges, the most commonly accepted treatment process, lime neutralization, is applied. Lime neutralization involves the addition of lime in a suitable form, either slaked or unslaked, to mine water to raise the pH of the discharge sufficiently to precipitate iron and aluminum hydroxides and subsequently to oxidize ferrous to ferric iron in an optimum environment. The cost of lime neutralization depends on many factors, including the volume of water, the concentration of pollutants, and the cost of available real estate for the construction of settling lagoons and sludge disposal sites.

In June of 1967, ECR initiated a research program to investigate the use of various sulfides for the treatment of mine water. The results of this work, which was conducted over a 15-month period under a grant from the Appalachian Regional Commission, indicated that the reaction of sulfides in mine water was such as to produce insoluble iron sulfides which could be recovered and utilized as a source of the sulfide reagent itself. Preliminary cost estimates suggested that, with the incorporation of sludge recovery and reagent recycling, the process would enable the treatment of mine water at lower cost than lime neutralization. Moreover, because of the small quantity of solid residue expected to be produced, the difficult problem of sludge disposal would be alleviated to a major extent. The results of this earlier program have been reported by Kawadski and Glenn. (16)

Subsequent to June, 1968, the research program was extended for a 12-month period under the current cosponsorship of the Federal Water Pollution Control Administration (FWPCA) and Bituminous Coal Research, Inc., with the objectives of continuing the development of the sulfide process for treatment of coal mine drainage utilizing a laboratory-

scale continuous flow system, and, using results of these studies, to make preliminary engineering evaluations and cost estimates on the process projected to a full industrial scale.

As a result of the earlier studies conducted for the Appalachian Regional Commission, a conceptual limestone-hydrogen sulfide (LHS) process for the treatment of mine water was developed. A schematic flow diagram of the process is shown in Figure 1. The process incorporated the use of limestone to increase the pH of the system to about 6, promoting the dissociation of hydrogen sulfide:

$$H_2S(aq) = H^+ + HS^-$$

$$HS^- = H^+ + S^{2-}$$

Subsequent addition of hydrogen sulfide resulted in the precipitation of iron as an insoluble iron sulfide:

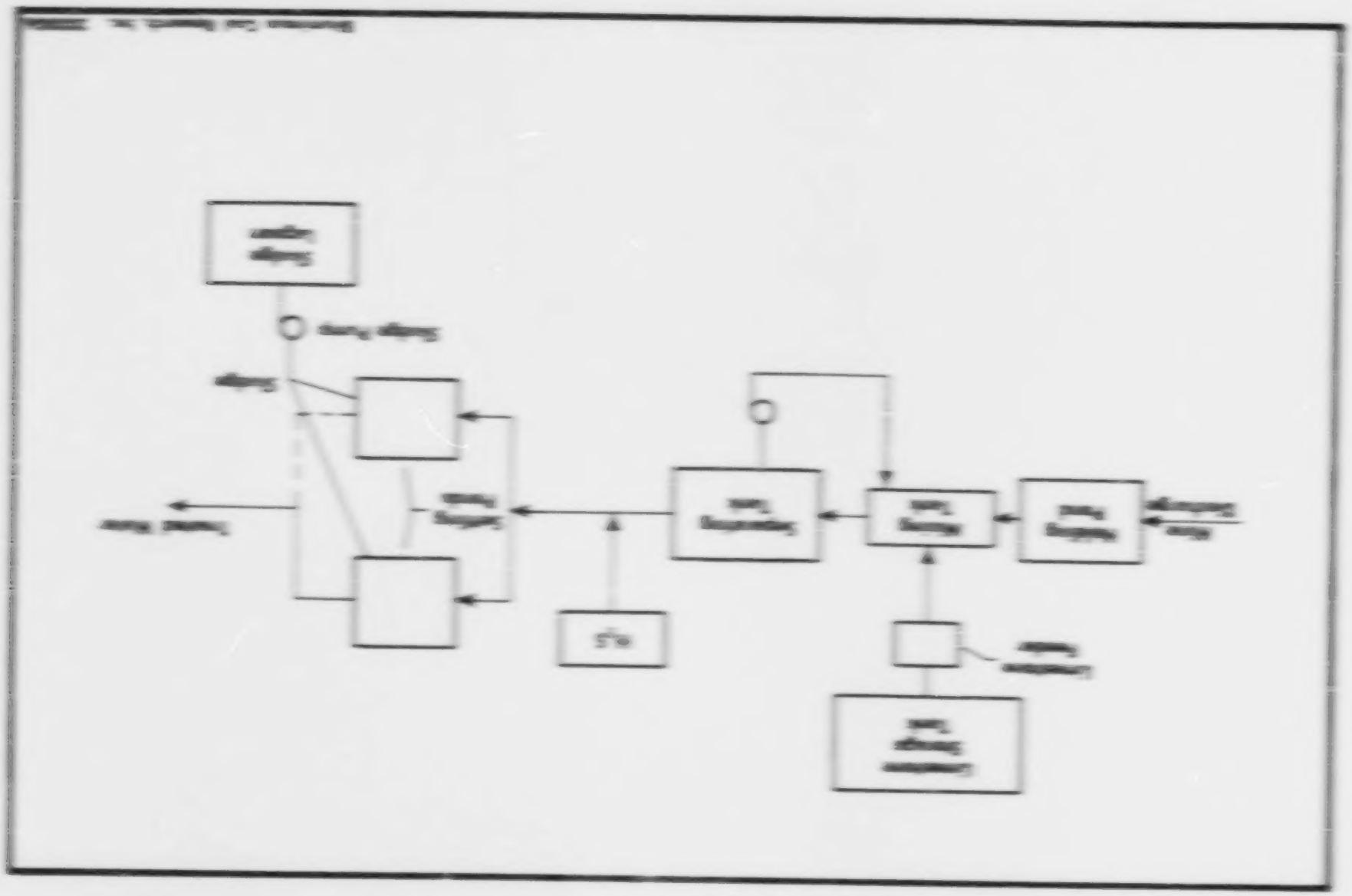
$$Fe^{2+} + S^{2-} = \underline{FeS}$$

This conceptual sulfide treatment process involved the various unit operations of pH adjustment, sulfide reaction, sludge separation, and sludge utilization. The flow diagram presented in Figure 1 provides for a system based on currently available technology; therefore, specific sludge separation devices are not indicated. A system for regenerating sulfide reagent from the sludge has not yet been developed and the diagram, therefore, shows sludge disposal as a present alternative.

Also as a result of the work sponsored by the Appalachian Regional Commission, a continuous flow test apparatus was designed and constructed at the BCR laboratory. This system, with a capacity of 1 to 5 gallons per minute, provided a means for evaluating the sulfide treatment process under dynamic conditions. A schematic drawing of the test apparatus is shown in Figure 2, and a photograph of the flow system in its original form is included as Figure 3. A detailed description of the continuous flow system equipment follows. It should be noted that this description applies to the equipment which evolved after several modifications (to be discussed in a later section) had been incorporated during the course of the work; consequently, there are some slight deviations from the representations given by Figures 2 and 3.

Reservoir: The reservoir has a total capacity of 210 gallons and consists of two Glascote glass-lined tanks[1] each having bottom discharge and lids. The tanks have 150 gallon and 60 gallon capacities.

[1] Mention of commercial products throughout this report does not imply endorsement by the Federal Water Pollution Control Administration.



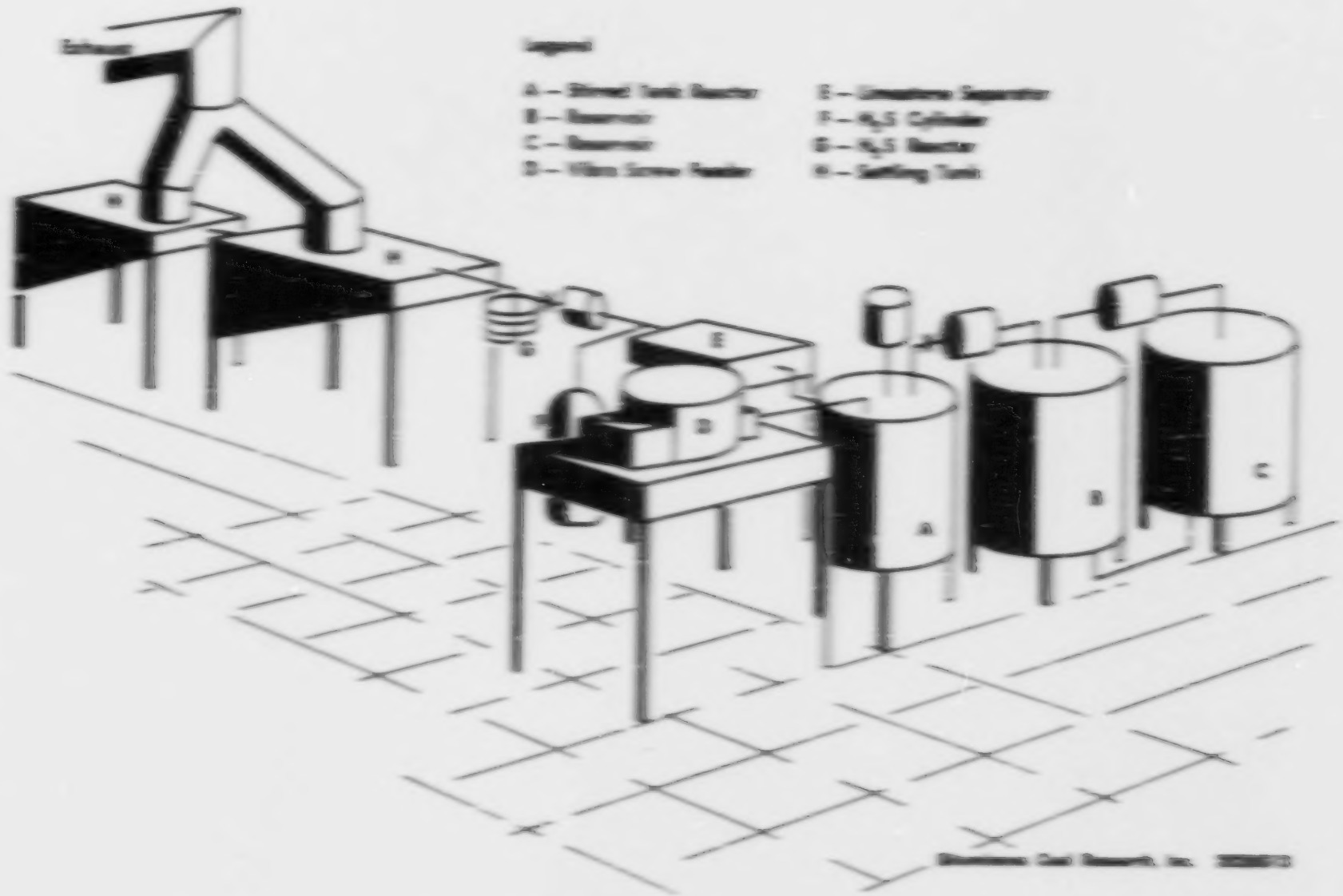


Figure 2. Continuous Flow Test Apparatus

Figure 2. General View of Continuous Flow System

Sample Cooling and Circulating System: A Forma "Forma-Temp" portable cooler can be used to maintain the sample at temperatures as low as 46 F. The cooler has a rated capacity of 4000 Btu/hr. Circulation of the sample between the two reservoirs is accomplished by use of a Gorman Rupp Model 11E90, 5600 Series pump, with a Gorman Rupp Model 12P00-91 oscillating pump used for priming.

IBM Reactor: The IBM reactor consists of a 60-gallon stainless steel tank equipped with four 3-inch vertical stainless steel baffles welded to the inner wall of the tank. Stirring is accomplished by use of a "Lightnin" Model MD-1A, 1/4 horsepower portable mixer. A 1/4-inch thick Plexiglas lid, containing a rectangular access port covered by a hinged Plexiglas panel, is bolted to the top of the 60-gallon tank. Rubber foam weather stripping (1/16-inch thick) is used as gasket material to seal the lid. The shaft of the "Lightnin" stirrer passes through a fitting packed with teflon cord, forming a water-tight seal. Mine water is pumped into the upper portion of the reactor from the reservoir with the aid of a Gorman Rupp Model 11E90, 5600 Series pump. The flow rate is controlled by a 1/2-inch Whitey Model 1RH0-316 stainless steel needle valve, and is measured by a Brooks Model 1305 Flowmeter. The hydrogen sulfide inlet, formed from 1/8-inch ID stainless steel tubing, enters near the top of the reactor and is directed down the inside and to the center near the bottom of the tank so that the gas is discharged just under the impeller blade. Gas flow rate is controlled and measured by means of a Brooks Model V 1300-01-FIB Flowmeter, equipped with a needle valve.

Limestone Feeder: Pulverized limestone is fed to the reactor by a Vibra Screw feeder equipped with a 1/4-inch diameter feed screw.

Settling Tanks: Two 30-gallon settling tanks in series are used to collect the sulfide sludge. These tanks are constructed of 316 stainless steel and are closed and vented to the outside air by ducting to a high capacity blower. Plexiglas covers enable visual observation of sludge settling behavior.

Piping: Stainless steel piping is in use throughout the system; however, large diameter Tygon tubing is used for flexible connection between the settling tanks.

Initial efforts under the present program were directed toward utilization of the continuous flow system for sulfide treatment experiments on mine waters of varying compositions. During the course of these experiments, however, various unforeseen difficulties were encountered which necessitated changes in the general direction of the work. These difficulties, and the attempts made to overcome them, will be described in subsequent sections of this report.

The work schedule covering the present program was revised by mutual agreement between BCR and the FWPCA at the end of the first eight months of the program, in consideration of certain findings during this period. In essence, these revisions involved a de-emphasis of the process engineering development work, and a return to more fundamental investigations of certain aspects relating to the basic chemistry of the sulfide treatment process for mine water. The revised work schedule resulting from these changes is shown in Figure 4.

Subsequent to the completion of the originally scheduled work program as revised (Figure 4), limited additional work on sludge characterization was undertaken by mutual agreement between the project cosponsors. The results of this work are discussed in later subsections entitled Tendency Toward Sludge Oxidation.

As work on the present program progressed, it became apparent that the reactions involved in the system were more complex than had been originally anticipated. Consequently, a more detailed literature search was initiated with the objective of acquiring an improved understanding of the chemistry of sulfide-iron reactions in solution. A number of the references obtained during this search would be of value in any future theoretical studies; these have been included, therefore, in Section 9, REFERENCES, under the subheading Additional References, Uncited.

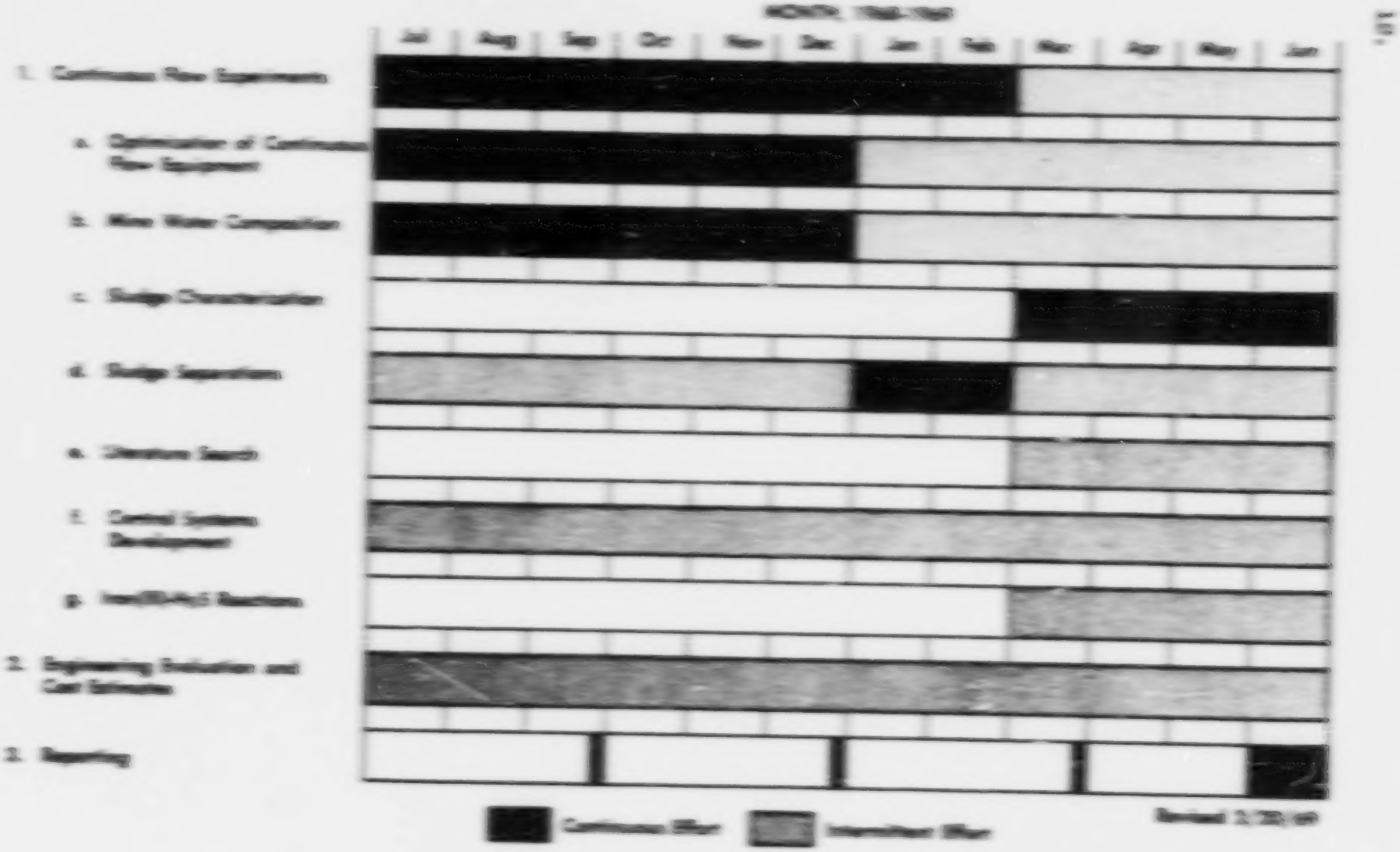


Figure 4. Schedule of Work--Sulfide Treatment of Acid Mine Drainage
(Grant No. 14010 DLC)

Section 3

EXPERIMENTAL

The major portion of the effort during the research program was devoted to determining the applicability of the limestone-hydrogen sulfide process for the continuous treatment of various types of mine waters. Accordingly, numerous continuous flow treatment experiments were conducted using mine waters of varying composition. At the same time, modifications in both equipment and procedure were made in an effort to refine the technique. These modifications were supplemented by smaller scale batch and continuous flow tests with the aid of a 5-gallon reactor.

During the development of the continuous flow treatment process, however, certain discordant results were obtained which could not be explained wholly on the basis of faulty technique or equipment design. Consequently, during the last four months of the program efforts were devoted essentially to studies of sludge formation, composition, and behavior. These studies involved brief and somewhat interrelated investigations of sludge chemical composition, physical properties, stability on exposure to air, electrophoretic mobility in the presence of various coagulant aids, and formation in the presence of hydrous ferric oxide.

This section deals with the experimental procedures and results obtained in each of the above-mentioned work areas.

Continuous Flow and 5-Gallon Batch Experiments

Reagents and Analytical Techniques

One of the initial purposes of the continuous flow experiments was to test the effectiveness of the sulfide treatment process on mine waters of varying composition. In selecting mine waters for treatment experiments, attention was given to parameters such as total iron concentration, ferric:ferrous iron ratio, and total acidity.

Four different mine waters were used in the earlier BMR continuous flow treatment experiments. Three of these were selected based on data presented in a report entitled "Dewitchley Creek Area of Pennsylvania" prepared for the Monongahela River Mine Drainage Remedial Project by the FWPCA, June, 1966, cited by Zawadski and Glenn. (16) The fourth site is near Belmont, Pennsylvania, about ten miles east of the BCR laboratory. The site locations, all in Westmoreland County, and the nature of mine water samples taken from them, are described briefly as follows:

South Greensburg (FWPCA No. 16-003): An inactive drift mine in Hempfield Township located on the north side of Pennsylvania T-681

northwest of its junction with Pennsylvania 6411. Samples are characterised by the usual absence of ferric iron and a fairly constant composition in spite of variations in flow rates.

Keystone (FWPCA No. 22-001): An inactive drift mine in Sewickley Township located near the junction of Sewickley Creek with the Youghiogheny River, approximately 200 feet west of Pennsylvania 6410A and 0.6 mile south of the junction of this road with Pennsylvania T-400. Samples are characterised by a relatively high ferrous iron and sodium content and by a relatively high pH. The ferric iron present tends to hydrolyse and precipitate fairly rapidly during storage of the mine water.

Tarrs (FWPCA No. 2-110): An abandoned mine site in East Huntingdon Township about 0.5 mile southwest of the town of Tarrs, Pennsylvania. Samples are characterised by a relatively high aluminum:total iron ratio and a relatively low pH, considering the rather high ferrous:ferric iron ratio.

Thorn Run Reservoir: A mine water holding lagoon in Salem Township about 0.1 mile east of Pennsylvania Route 66 and 1.1 miles north of the junction of this road with U.S. Route 22. Samples are characterised by a high ferric:ferrous iron ratio and low pH. The composition of the mine water varies widely depending on flow rate, suggesting a dilution effect from surface water run-off during periods of rainfall.

Representative analytical data for these four samples are shown in Table 1.

In the later continuous flow tests, as well as batch tests and sludge characterization studies, mine water from the South Greensburg site was utilised almost exclusively. Because of the usual absence of ferric iron in fresh samples and its relatively constant composition, the South Greensburg mine water was employed in effect as a "control" sample throughout the investigation.

The limestone used throughout the course of the investigation, designated as BOR No. 1809, was obtained from the West Winfield Lime and Stone Company, West Winfield, Butler County, Pennsylvania. This material is a deep-mined, high calcium limestone containing about 89 percent calcium oxide by weight of ignited (900 C) sample, and has been found by tests conducted under another BOR project to be a relatively effective neutralising agent compared with other limestones of similar composition (unpublished data). Preliminary continuous flow tests were conducted using limestone which had been ground from lump size to 80 percent by weight minus 200 mesh. In later work, the same limestone was obtained as the agricultural grade, then ground and sieved to minus 325 mesh. In all but a few 5-gallon batch tests, the amount of

pulverized limestone employed in treatment experiments was twice the stoichiometric requirement based on mine water total acidity.

Reagent grade hydrogen sulfide used in all tests was obtained from The Matheson Company in a pressurized cylinder. Gas flow rate was measured with the aid of a Brooks "Rho-Mate" flowmeter calibrated to read directly in standard liters per minute of gas with a specific gravity of 1.17 at S.T.P. (i.e., hydrogen sulfide). The flowmeter calibration was checked occasionally using air and a wet-test meter, with appropriate density corrections. Ordinarily, hydrogen sulfide was added in an amount equal to the exact stoichiometric requirement based on the following reactions:

$$Fe^{2+} + H_2S = FeS + 2\,H^+$$

$$2\,Fe^{3+} + H_2S = 2\,Fe^{2+} + 2\,H^+ + S^0$$

For reasons which will become apparent later, it was sometimes necessary to back-calculate the hydrogen sulfide stoichiometry after a treatment experiment due to changes in iron concentration and/or oxidation state during storage of the mine water samples. In these instances, the amount of hydrogen sulfide employed proved to be some multiple or fraction of the exact stoichiometric requirement.

Ferrous iron concentration was determined by the colorimetric method using ortho-phenanthroline. Sample absorbance was measured at 510mμ with the aid of a Beckman Model DB spectrophotometer. Unless indicated otherwise, ferrous iron analyses were conducted on filtered samples.

Total iron was determined by emission spectrographic analysis using a solution technique. This same procedure was used for the determination of other cations of interest. Concentrations of these cations (aluminum, calcium, magnesium, manganese, silicon, and sodium) are expressed throughout this report as milligrams of the elemental species per liter.

Total acidity was determined by titration to pH 8.2 with 0.1N sodium hydroxide of the solution, previously treated with hydrogen peroxide solution, boiled, and cooled. All acidity values reported herein are expressed as milligrams per liter calcium carbonate equivalents.

Experimental Procedure and Results

The experimental procedure for continuous flow tests was varied considerably in the early stages of the investigation as changes in equipment and technique were incorporated. In the first few flow experiments, pulverized limestone was mixed with the mine water in a separate vessel before the introduction of hydrogen sulfide to the suspension. This approach proved to be unsatisfactory since there was no provision for mixing downstream from the point of hydrogen sulfide

introduction, and pH recovery after hydrogen sulfide addition was too slow.

After various mechanical problems had been encountered (see below), the 60-gallon mixing tank was converted to an enclosed stirred reactor with the addition of a Plexiglas lid and appropriate inlet and outlet lines. This innovation permitted simultaneous addition of limestone and hydrogen sulfide to the mine water with high-speed stirring, and provided for more efficient use of the reagents.

The procedure ultimately adopted for continuous flow treatment experiments is as follows: Mine water samples were collected in the field in four plastic-lined 55-gallon drums and, immediately upon return to the laboratory, were transferred to the holding tanks. During storage, samples were maintained at a temperature in the range 8 to 10 C (46 to 50 F) with a portable immersion cooler to minimize iron oxidation and precipitation. Samples of the raw mine water were taken immediately for as-received determinations of pH, acidity, ferrous and total iron, and in some cases, sulfate concentration. In addition to total iron, concentrations of aluminum, calcium, magnesium, manganese, silicon, and sodium were ordinarily determined by the emission spectrographic technique on raw mine water samples.

At the start of a continuous flow treatment run, the 60-gallon reactor was first charged with 50 gallons of raw mine water. The entire amount of limestone required by the 50-gallon sample was weighed and added to the contents of the reactor just before mixing and hydrogen sulfide flow commenced. The system was then operated in this "batch configuration" for a 30-minute period. At the end of this time period, mine water influent and treated effluent flows were started at the rate of 1 gallon per minute, continuous limestone feeding was commenced, and the system was operated in a "flow configuration" for the duration of the run. After the system was operating in the "flow configuration," samples were taken immediately from the reactor and at subsequent time intervals from the first settling tank for pH measurement and iron analyses. In addition, after all flow had ceased in the system, samples were taken periodically from the settling tanks for the purpose of determining changes in pH and dissolved iron content in the treated effluent with time.

The results of the earlier continuous flow runs, in terms of the degree of iron removal achieved, tended to be erratic and somewhat inconclusive. This was due in part to mechanical difficulties, as indicated earlier, most of which gave rise to problems in maintaining smooth flow and adequate hydrogen sulfide-liquid mixing within the system. However, based on discoveries made later in the investigation, it is likely that the unsatisfactory iron removals in earlier runs were also influenced by changes in mine water composition prior to treatment.

The results of these preliminary flow runs are typified by the data in Table 8. As indicated therein, the iron removals effected were only about 60 to 70 percent in all cases.

These preliminary continuous flow experiments were followed by a series of 5-gallon batch tests, designed to provide closer insight into the fate of dissolved iron during treatment through closer control of experimental conditions. The batch tests were conducted in an enclosed, stirred reactor built from a 5-gallon polyethylene screwcap bottle. Stainless steel tubing was used to provide a mine water inlet near the top and a hydrogen sulfide inlet at the bottom of the vessel.

In a typical batch treatment experiment, a 5-gallon sample of mine water was mixed with the requisite amount of limestone for 15 minutes, followed by introduction of hydrogen sulfide over a 5-minute period. Samples were withdrawn from the tap at the bottom of the stirred reactor, both before and for some time after hydrogen sulfide addition, for pH and ferrous iron analyses.

Results of these 5-gallon batch tests are illustrated graphically in Figures 5 and 6. The results shown by Figure 6 were obtained after the hydrogen sulfide flowmeter was recalibrated and are, therefore, probably more meaningful. The runs reflected by Figure 5 were conducted using South Greensburg mine water with a pH of 5.80, 111 ppm ferrous iron, 0 ppm ferric iron, and 267 ppm total acidity; those represented by Figure 6 were conducted using mine water from the same source with a pH of 5.84, containing 121 ppm ferrous iron, 0 ppm ferric iron, and 260 ppm total acidity.

These batch tests were followed by conversion of the 60-gallon mixing tank to an enclosed, combination limestone-hydrogen sulfide reactor and the conduct of five additional continuous flow experiments by the procedure described earlier. During these experiments it was discovered that significant amounts of ferrous iron were undergoing oxidation even during brief storage periods of approximately two hours prior to treatment. Evidently, this problem could not be avoided even when the mine water samples were collected in the field, transported to the laboratory, analyzed, and utilized in the flow system all within an 8-hour period. Consequently, although preliminary hydrogen sulfide feed requirements had been calculated based on the "as received" analyses of the mine water, in each run it was necessary to back-calculate the stoichiometric amount of hydrogen sulfide used after the run had been completed, based on updated analytical results for ferrous and total iron on samples taken during the run itself.

This situation is reflected in Table 1, which summarizes the pertinent analytical data for the five continuous flow experiments. These data show that the original mine water composition was essentially the same in each of the runs. Furthermore, the mine water was essentially free of ferric iron at the time of collection. These results were consistent with those obtained earlier for this particular mine water.

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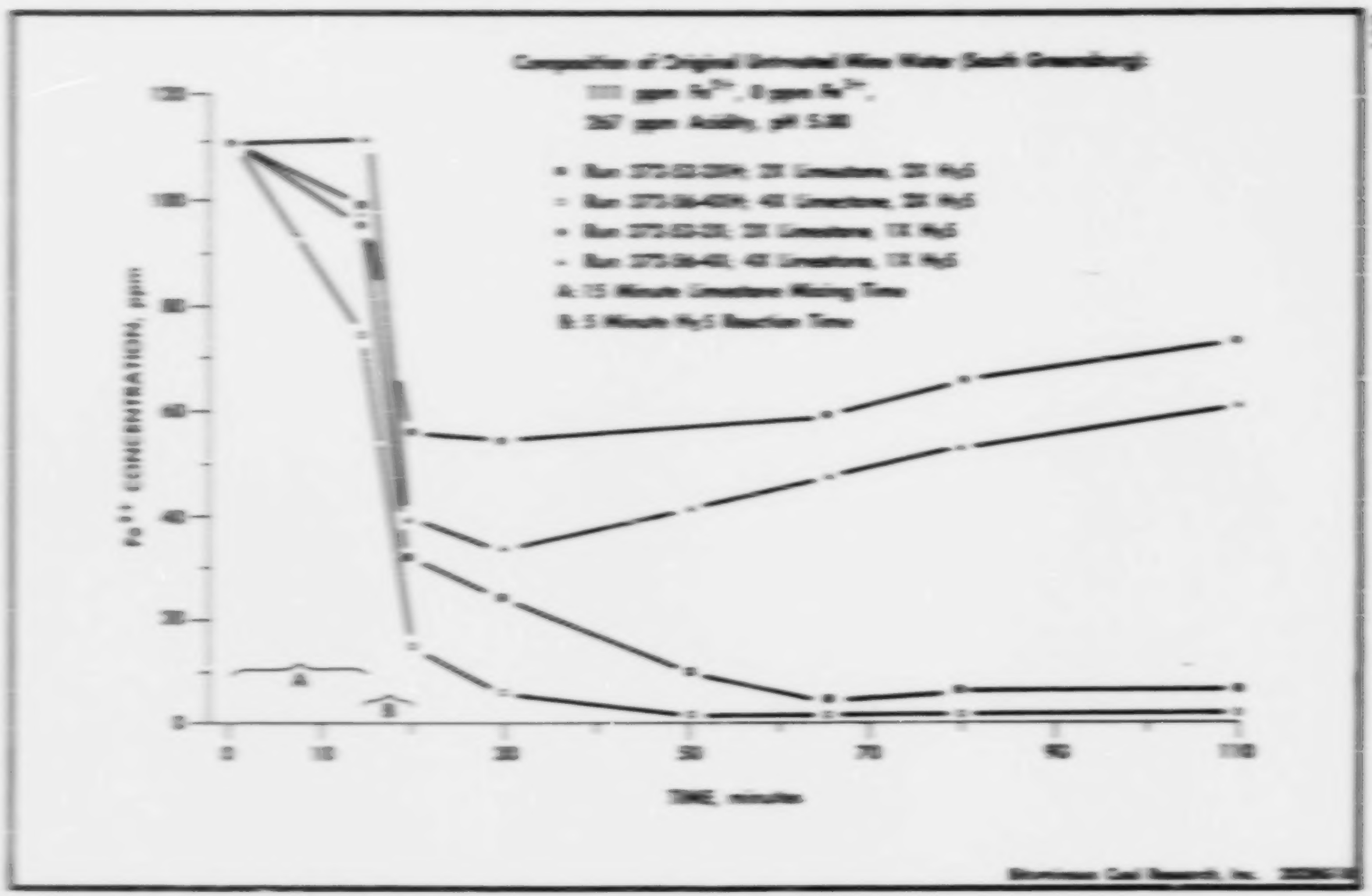
Composition of Original Untreated Mine Water (South Greensburg):
1111 ppm Fe^{2+}, 0 ppm Fe^{3+},
267 ppm Acidity, pH 5.58
A: 15 Minute Limestone Mixing Time
B: 5 Minute H_2S Reaction Time
Fe^{2+} CONCENTRATION, ppm
TIME, minutes

Figure 5. Change in Residual Dissolved Iron Concentration with Time: Sectional Reactor 3-gallon Batch Tests

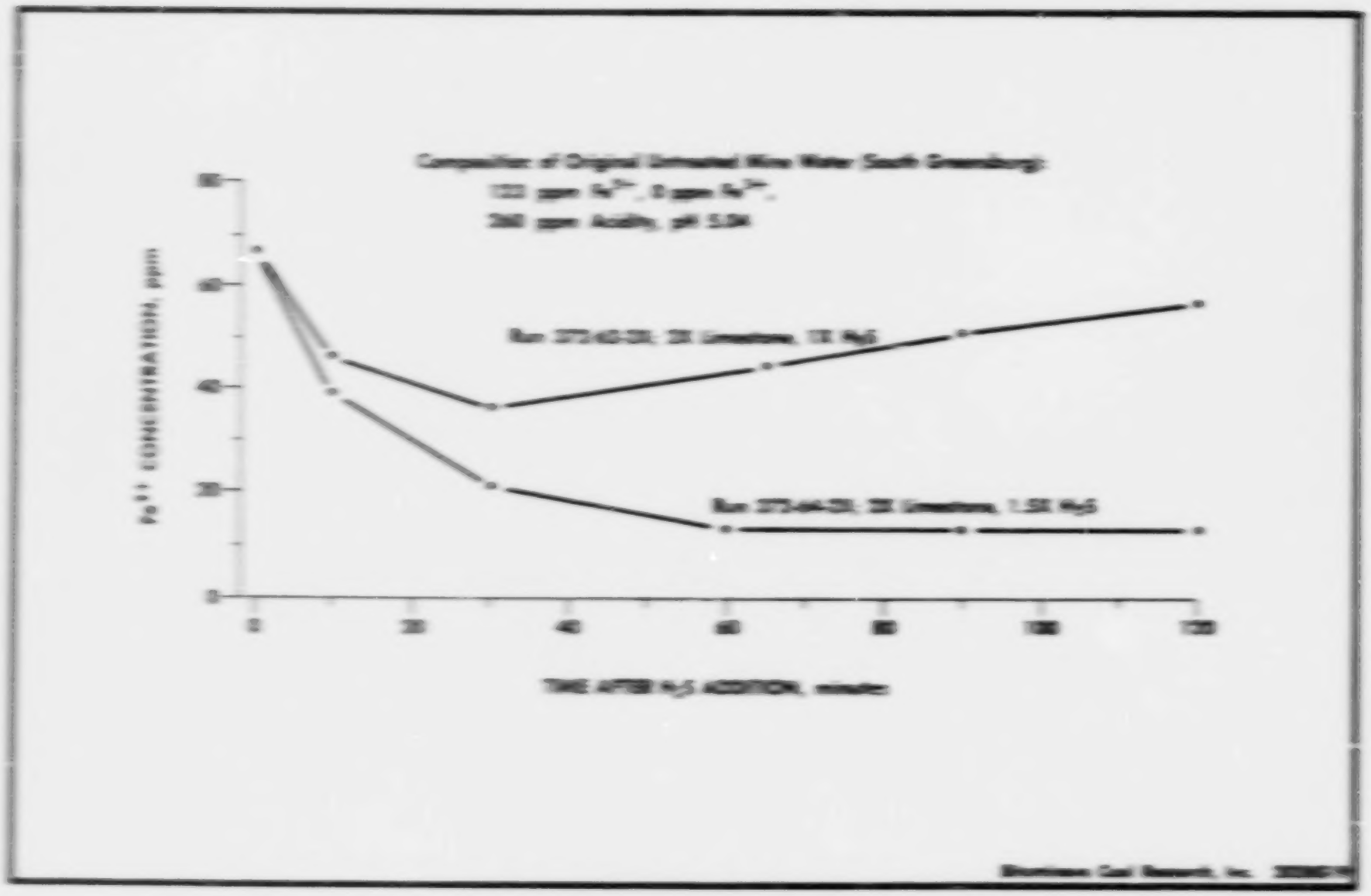

Figure 6. Change in Residual Dissolved Iron Concentration with Time after H2S Addition; Reducing Reactor Supplies Both Tests

With the exception of the results from Run 170-70, the data indicate that about 85 to 97 percent of the ferrous iron in the mine water underwent fairly rapid oxidation during storage of the sample prior to treatment, and there is some evidence (Run 170-71) that no appreciable further ferrous iron oxidation occurred during a subsequent prolonged storage period (with cooling) up to two days. This seemingly anomalous behavior may be explained by the fact that, as oxidation and hydrolysis of iron occurs, the pH of the system decreases, thereby decreasing the rate of ferrous ion oxidation to a point that the rate becomes negligible and the system is in equilibrium. In addition, it should be recognized that mine water samples were stored with cooling in covered tanks, thereby limiting the access of air to the samples. If one assumes that diffusion of oxygen through the air-liquid interface was the rate-controlling step in the iron oxidation process, then it seems reasonable that ferrous iron oxidation should either cease or proceed at a negligible rate once dissolved oxygen and oxygen in the small air spaces at the tops of the storage tanks was depleted. Based on the analytical data (Table 2), one would expect the Keystone and, possibly, the Tarra discharges to behave in a similar fashion. Unfortunately, however, usage of these two mine waters was limited in the present study, and the data obtained therefrom are insufficient for the purpose of comparison.

The data in Table 3 show a rough correlation between the amount of hydrogen sulfide employed and the amount of ferrous iron remaining in the treated effluent. This trend is illustrated more clearly by Figure 7, which shows the change in ferrous iron concentration in the effluent with time at the different hydrogen sulfide feed levels. Concerning Figure 7, it should be pointed out that time zero indicated thereon corresponds to the time at which mine water flow was begun in the system. As explained earlier, this point in time was preceded by a 90-minute mixing period during which the system was operating in a "batch configuration" with only hydrogen sulfide flow into the mixing tank containing the initial 50-gallon mine water-limestone charge. The ferrous iron concentration at time zero was determined on a sample taken from the reactor itself; all subsequent samples were taken from the first settling tank. The solid-line portions of the curves in Figure 7 correspond to the time periods during which flow was occurring in the system. The dashed-line portions correspond to the time periods after flow ceased, during which the treated effluent was allowed to stand undisturbed in the settling tanks. The "final" treated effluent analyses, shown in the extreme right-hand columns of Table 3, correspond to the last points on the curves of Figure 7 before the breaks indicating the overnight settling periods.

During the course of the continuous flow test work a number of improvements were made in the design of the system. A few of these were relatively minor, such as the installation of drains from all holding tanks and the addition of a glass tube level indicator on the mixing tank. The major modifications, resulting from recurring

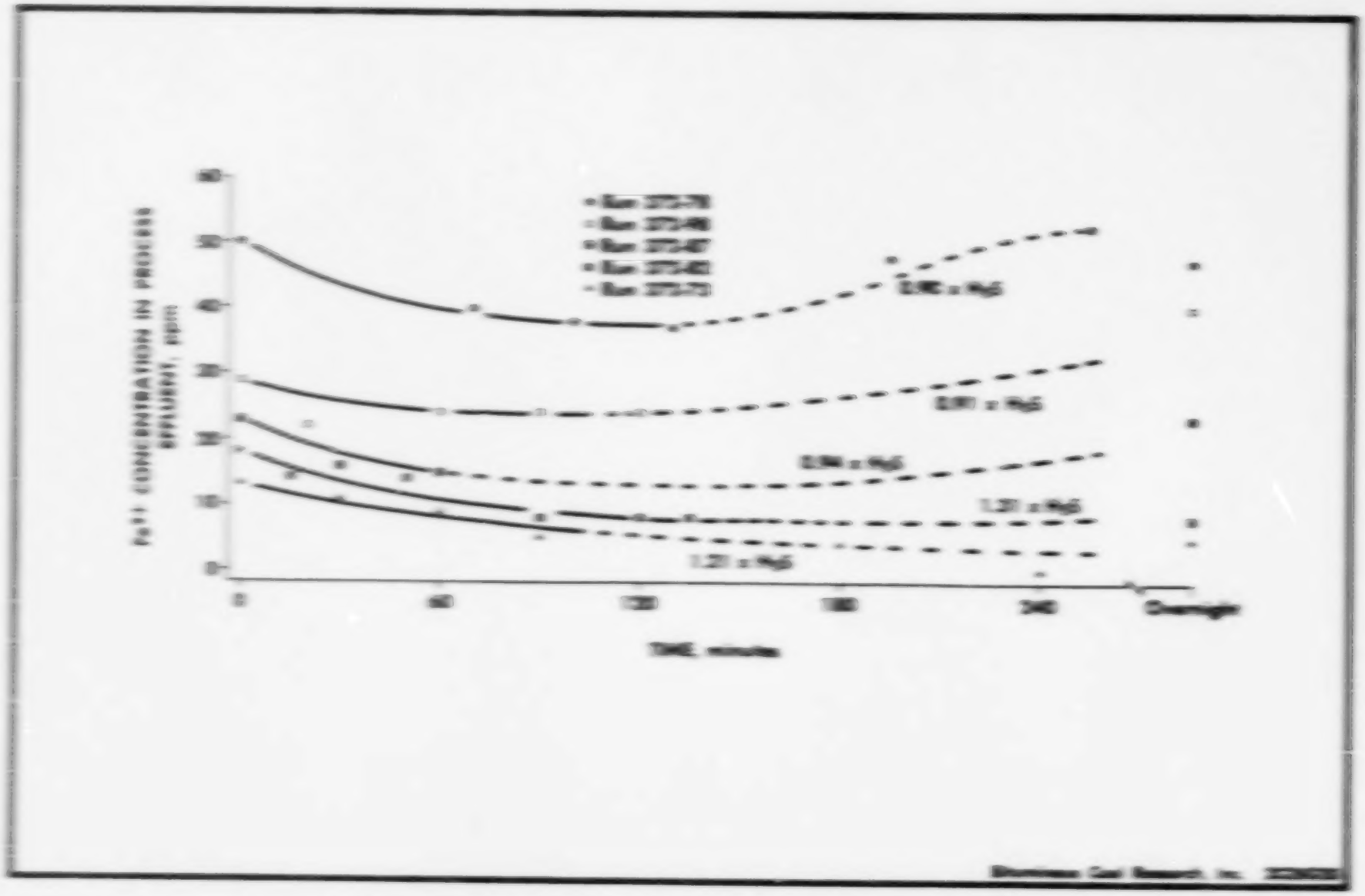

Figure 7. Continuous Flow Runs With 60-gallon UIS Reactor: Change of Fe^{3+} Concentration in Process Effluent with Time

mechanical difficulties encountered, are described in the following paragraphs.

In the system as originally designed, the treated suspension containing excess limestone particles was transferred by a small centrifugal pump through a flowmeter into the first settling tank. This led to frequent problems due to clogging in the flowmeter and regulating valve, resulting in erratic flow downstream from the mixing tank. This difficulty was overcome by removing the pump and flowmeter, raising the mixing tank to a higher elevation, and installing a length of 1/2-inch ID stainless steel pipe directly from the bottom of the mixing tank to the settling tank inlet to permit gravity flow of the process effluent.

The limestone screw feeder installed in the continuous flow system was originally purchased for another BCR project and was not designed to provide directly the low feed rates (1.5 to 2.0 grams per minute) required in the flow tests. It was found necessary to calibrate the feed rate by a trial and error method prior to each run, and this erratic response of the feeder led to uncertainties concerning control of limestone addition. Various remedies were attempted, and other types of feeders were evaluated during the course of the investigation. Rather late in the experimental work, however, it was discovered that replacement of the 1/2-inch feed auger with one of 1/4-inch size (originally believed to be unavailable from the manufacturer) resulted in satisfactory, controllable feed rates for the pulverized limestone.

Various methods of hydrogen sulfide introduction were attempted early in the investigation. The original arrangement wherein hydrogen sulfide was admitted through a tee ahead of a coiled section of tubing (Figure 2) was wholly unsatisfactory due to insufficient reaction time, inadequate gas-liquid mixing, and problems with back-pressure flow of liquid into the hydrogen sulfide flowmeter. Admitting the hydrogen sulfide through a fritted glass diffuser into a stirred compartment at the head of the first settling tank resulted in only a slight improvement; difficulties due to inadequate gas-liquid contact time and loss of hydrogen sulfide by diffusion were still encountered. The technique which eventually proved satisfactory involved admitting the gas through an open pipe (1/8-inch ID stainless steel tubing) directly under the impeller of the high-speed mixer. Direct observation confirmed that the hydrogen sulfide, which is relatively soluble to the extent of 2580 cc in 1000 cc of water at 20 C (10), apparently dissolved completely during stirring before it had a chance to escape through the air-liquid interface.

Early in the research program, the following equipment manufacturers were contacted concerning hydrogen sulfide feed control instrumentation:

The Foxboro Company, Foxboro, Massachusetts
Honeywell, Minneapolis, Minnesota
API Instruments Company, Chesterland, Ohio
ITT Barton, Controls & Instrument Div., Monterey Park, California

Among these, the only response during the course of the work was from a representative of Honeywell who indicated that his company does not manufacture analytical control devices for hydrogen sulfide. He suggested, however, that it might be possible to couple a gas flow measuring device such as Honeywell's integral orifice assembly with a hydrogen sulfide-sensing device such as the "Toxgard," manufactured by Mine Safety Appliances Company (MSA), Pittsburgh, Pennsylvania. The latter instrument is an amperometric-type device capable of detecting hydrogen sulfide in the range 0 to 50 ppm.

In a subsequent discussion, a representative of MSA advised that the "Toxgard" would not be suitable as a hydrogen sulfide feed control device, either alone or in conjunction with some type of flow regulator. He explained that the "Toxgard" is designed primarily as a monitoring instrument to warn of hazardous levels of toxic gases within a working area (i.e., it is not designed for use on process streams). The MSA representative suggested that a technique involving continuous chromatography or ultraviolet spectroscopy might be the best approach for our desired application; however, both analytical techniques require rather expensive instrumentation.

In summary, the limited response to our inquiries concerning hydrogen sulfide feed control instrumentation was rather indifferent, and indicated that control instrumentation for use with our specific application was not commercially available. In view of these findings, therefore, it was felt that the development of such control instrumentation would be an undertaking beyond the scope and resources of the present project.

Sludge Characterization Studies

At the inception of the current research program, essentially no precise information was available on the chemical composition or physical properties of the freshly formed, black precipitate produced by the lime treatment of mine water. Under the previous program (for the Appalachian Regional Commission), some data were accumulated on sludge samples dried under nitrogen at 100 C for 1 to 2 hours. For example, sulfur:iron ratios on sludges treated in this manner were found to be in the range 1.4 to 1.9; and among the iron sulfide species identified by x-ray diffraction analyses of the pyrolyzed samples were FeS, FeS_2, and Fe_3S_4.

There was some doubt as to whether these results were indicative of the actual composition of the freshly formed sludge. For this reason, and in an effort to better understand the phenomena observed during the continuous flow experiments, sludge characterization studies were initiated on a limited scale during the later stages of the investigation.

Experimental Procedure and Results

Chemical Properties

A procedure was developed for the determination of iron and sulfide sulfur on sludges formed during the IMM treatment process. The procedure was based on decomposition in 6N hydrochloric acid of the filtered, washed sludge in a closed system. An all-glass apparatus connected with standard taper joints and short lengths of Tygon tubing was used in these studies.

A sample of the sludge, filtered on a 0.2μ pore size Millipore filter disk and washed with deionized water, was wrapped in a small piece of aluminum foil and immediately transferred to a 50-ml boiling flask containing 25 ml 6N hydrochloric acid and equipped with a magnetic stirring bar. The reaction flask was connected with two gas bubbler tubes in series each containing a solution of 1M cadmium chloride. The entire system was purged with prepurified nitrogen gas for at least 1/2 hour before the sample was introduced.

As the sludge sample decomposed in the stirred, acidic solution, hydrogen sulfide liberated during the reaction was swept with nitrogen into the bubbler tubes wherein cadmium sulfide precipitated. The decomposition was driven to completion by heating the acidified solution to boiling, after which the contents of the flask were allowed to cool, diluted to 250 ml, and analysed for total iron by the emission spectrographic technique. The cadmium sulfide precipitate was filtered in a fine-porosity fritted glass crucible, washed, dried at 400 C for 2 hours, and weighed.

During the development of the procedure and analyses of actual sludge samples, control runs with pure ferrous sulfide were conducted for comparison of the results. In addition, a blank experiment with aluminum foil alone in the system showed that no measurable iron was being contributed to the solution by the aluminum itself.

The results of sulfide sulfur and iron analyses conducted on sulfide sludges and pure ferrous sulfide by the above-described procedure are given in Table 4. The sulfide sludge samples were all prepared by treatment of South Greensburg mine water in batch experiments using the exact stoichiometric requirement of hydrogen sulfide. Each of these batch tests involved the use of twice the stoichiometric requirement of limestone except for Test No. 389-48, in which 1N sodium hydroxide was used for reasons to be discussed later. In addition, in all tests involving sulfide sludge samples except Test No. 389-17, the original mine water sample was filtered through 1.0μ pore size Millipore filter disks immediately prior to treatment. This was done to reduce interferences due to suspended hydrous ferric oxides in the mine water (also to be discussed later).

৩৫.৩	৯৫.৩	৫৫.৩	কঠিন কয়লা	১৯-২৫
৯৮.৩	৯৯.৩	৫৪.৩	কঠিন কয়লা	১৯-২৫
৭৫.৩	৯৫.৩	৯৫.৩	চন্দ	৫৮-২৫
৫৫.৩	৫৯.৩	৫৫.৩	কঠিন কয়লা	১৫-২৫
৫৫.৩	৫৫.৩	৫৫.৩	চন্দ	৫৮-২৫
৫৫.৩	৫৫.৩	৫৫.৩	কঠিন কয়লা	৫৫-২৫
৫৫.৩	৫৫.৩	৫৫.৩	চন্দ	১৫-২৫
৫৫.৩	৫৫.৩	৫৫.৩	চন্দ	১৫-২৫
৫৫.৩	৫৫.৩	৫৫.৩	চন্দ	১৫-২৫
৫৫.৩	৫৫.৩	৫৫.৩	চন্দ	১- ২৫

মোট কী ক্ষেত্র	কয়লার উপর ৩য় প্রান্তিকের		কয়লার ধরন	কয়লা খনি
	খরচ	কর		

ছক ৮. ২০১৯ সালের ৩য় প্রান্তিকে এক বছর মেয়াদের ৩ ধরনের কয়লার
এক টনের হিসাবের ধরন

X-ray diffraction analyses were conducted using the powder camera technique and a scanning diffractometer, each employing copper K_α radiation. Outside services were required for the use of the latter instrument. It was found that sludge samples, which ordinarily underwent oxidation rather rapidly after exposure to air, could be preserved in their original state for at least several hours by drying them in a vacuum oven at room temperature.

X-ray diffraction analysis was conducted on the sulfide sludge from Test No. 83-42. The sludge was prepared specifically for this purpose, and x-ray analysis was accomplished immediately after preparation while the vacuum-dried sludge was still black in color. A sample of powdered, pure ferrous sulfide was also submitted as a reference material.

The peaks of the x-ray pattern for the ferrous sulfide reference sample corresponded closely in position and intensity to those for ordered ferrous sulfide (Troilite; Powder Diffraction File card No. 4-0835). For the sulfide sludge sample, all peaks in both the powder photograph and the recorded diffractogram were assignable to either calcite ($CaCO_3$) or α-quartz (SiO_2), both compounds presumably originating from unreacted limestone in the sludge sample. Although it was possible that the 100 percent peak of ferrous sulfide at d=2.09 A was masked by a relatively strong 18 percent peak of $CaCO_3$ appearing in the diffractogram at d=2.08 A (reference value d=2.093 A), a numerical analysis of the relative peak intensities indicated that this was not so.

To avoid this possible interference due to the presence of calcite in the sample, the experiment was repeated using 1N sodium hydroxide during sludge preparation. The mine water was maintained at pH 6 by incremental additions of the base during hydrogen sulfide addition. X-ray diffraction of the resulting black, vacuum-dried solids failed to produce any definitive pattern.

Physical Properties

Again, only limited data were available on the physical properties of the freshly formed sludges at the inception of the current research program. As sludge chemical properties began to take on added importance, it was decided to investigate briefly two selected physical properties of the sludge, namely, solids content and settled sludge volume.

Two experiments on comparison of sludge volumes and solids contents were conducted based on lime, limestone, and BM treatment of South Greensburg mine water, according to the following procedure.

Concurrent with the continuous flow LMH treatment experiment, two batch samples of the raw mine water were taken for lime and limestone neutralization tests. Sufficient 30 percent hydrogen peroxide solution was added to each sample to oxidize ferrous iron, then one sample was neutralized with twice the stoichiometric requirement of limestone (-325 mesh BCR No. 1809), and the second sample was neutralized with an amount of 10 percent hydrated lime slurry sufficient to raise the pH to 7. The limestone-treated suspension was stirred for 30 minutes, and the lime-treated suspension was stirred just long enough to effect the desired neutralization and precipitation of iron. The final pH of both suspensions was about 7. These samples, as well as a sample taken during the LMH treatment experiment, were transferred to 1-liter Imhoff cones and sludge volumes were measured after overnight settling. The supernatant liquid was then decanted from each sample by careful siphoning to avoid disturbing the settled solids, and portions of the gravity-settled solid material were transferred to small, tared beakers.

The solids were weighed, dried at 110 C for 1 hour, allowed to cool, and weighed again. In addition, similar weighed samples of the settled sludge were washed on No. 42 Whatman filter paper, and the residue obtained after evaporation of the filtrate was weighed. In this manner, the contribution due to dissolved solids in the original solids content determination could be ascertained.

The results of sludge volume comparison tests and solids content analyses, conducted during continuous flow LMH treatment experiments 170-62 and 170-63, are shown in Table 5. As indicated therein, fairly good agreement between the results of the two tests was obtained in most cases.

Tendency Toward Sludge Oxidation

Rather early in the experimental work, it was observed that damp sludge filter residues resulting from the LMH treatment of mine waters tended to change color from black to rust-orange within minutes after exposure to air. Scheduling arrangements involving the process development and continuous flow testing phases of the project did not permit a fuller investigation of this phenomenon until much later in the experimental studies, however. This aspect of sludge behavior was investigated briefly in the following experiment:

A sulfide sludge was prepared by the LMH treatment of South Greensburg mine water in the 5-gallon reactor. Two samples of the suspension were withdrawn 45 minutes after the reaction and filtered on 0.05µ Millipore paper.

The first filter cake was washed with dilute hydrochloric acid, leaving a brown residue which was found to be a mixture of sulfur and quartz. The sulfur presumably arose from hydrogen sulfide reduction of ferric iron, known to be present in the mine water prior to treatment, and/or partial sludge oxidation before filtration.

The second filter cake was washed with water alone and allowed to air dry at room temperature, during which time it changed from black to a rust-brown color. X-ray analysis of a portion of the dried solids revealed sulfur and calcium carbonate; no lines due to iron compounds could be identified. The remaining rust-brown solids were washed with dilute hydrochloric acid, leaving a substantial amount of a grey residue identified as sulfur. The acidified washings were found to contain 1 ppm ferrous iron, 16 ppm ferric iron, and no sulfate.

The ease of sludge oxidation was demonstrated dramatically early in the investigation, when attempts were made to prepare x-ray specimens by washing filtered sludge samples with a water-miscible, low-boiling solvent (i.e., acetone) to effect rapid room temperature drying. For example, the sludge resulting from a continuous flow IBM treatment experiment using South Greensburg mine water was allowed to stand overnight in the settling tanks. On the following day the relatively clear supernatant liquid was decanted from one of the tanks and a portion of the sludge, still jet black in color, was filtered in a medium frit glass filter funnel. The damp filter cake was washed several times with acetone and then pulverized inside the funnel to a dry, black powder by grinding with a glass rod.

The bulk of the powder was then poured out onto a clean sheet of paper for subsequent transfer to a plastic vial. Within 10 seconds, however, a strongly exothermic reaction occurred which caused the paper to smolder and char. The powder changed color from black to dark brown during this reaction, and a pungent odor, possibly that of sulfur dioxide, was detected.

The experiment was repeated later on sludge from the IBM treatment of a different (Keystone) mine water. A portion of the filtered sludge washed only once with acetone and ground to a granular powder failed to produce the expected reaction. However, a second portion washed four times with acetone and ground to a fine, dry powder underwent the exothermic reaction about ten minutes after being placed in contact with the paper. The powder was immediately placed in a small beaker, and the beaker became quite hot to the touch. There was no evidence of a sudden or violent decomposition reaction, however.

In both cases, small amounts of the acetone-washed filter residues (which may or may not have undergone the exothermic reaction exhibited by the bulk of the powder) were recovered and submitted for x-ray diffraction analyses. Only limestone residues (calcite, silica) and possibly calcium sulfate were identified from the x-ray patterns; no lines assignable to iron compounds were present. Also, in both cases, the powders continued to lighten in color from dark brown to a rust- or chocolate-brown during exposure to air for several days.

The pyrophoric behavior of the IBM sludge was demonstrated again, somewhat unexpectedly, during later attempts at solids content determinations. A sample of the sulfide sludge, filtered on Whatman No. 40

paper, was placed in an oven for drying at 110 C. Shortly afterward, smoke was observed coming from the oven. Inspection of the oven contents revealed that the portion of the filter paper which had been covered by the sludge was completely disintegrated; only a black ash remained. Thus, there is evidence that the sulfide sludge, wet with water alone, will undergo the exothermic reaction when dried under conditions of moderately elevated temperature. This finding tends to preclude the possibility, considered when the phenomenon was first observed, that residual acetone may have initiated the exothermic reactions of sludges dried at room temperature.

One possible explanation for the pyrophoric properties of the sludge, observed under accelerated drying conditions, involves the occurrence of finely divided elemental iron (formed by reduction of ferrous ion in the presence of hydrogen sulfide) and its reaction with sulfur residues in the sludge. Such a reaction is known to be strongly exothermic, at least when initiated by heating. To explore this possibility further, limited additional work was undertaken with the objective of confirming the presence or absence of metallic iron in the pyrophoric sulfide sludge.

The overall procedure involved the precipitation and characterization of sulfide sludges, formed by the addition of hydrogen sulfide to synthetic and actual mine waters in the presence of an alkali. Tendencies toward pyrophoric behavior were observed after sludge samples were filtered, washed with acetone, and dried at room temperature. Efforts to separate and identify iron in the precipitates involved employment of the following techniques: X-ray diffraction analyses of sludges and sludge-iron powder admixtures, centrifugation tests, and tests for magnetic behavior of gravity-settled and centrifuged solids. In addition to the experimental work, a brief revier of pertinent literature was conducted to determine whether reduction of iron to the elemental state is thermodynamically possible in aqueous systems, and to determine if other researchers have encountered similar pyrophoric behavior with iron sulfide mixtures.

A synthetic ferrous sulfate solution (1000 ppm ferrous ion) acidified to pH 3.0 with sulfuric acid was employed for most experiments in this series. All experiments were conducted at room temperature on 2-liter aliquots of the synthetic or natural mine water. The reaction vessel consisted of an open 4-liter beaker equipped with a magnetic stirring bar, a fritted gas dispersion tube for hydrogen sulfide introduction, and electrodes for pH measurement. In every case, hydrogen sulfide was added at twice the stoichiometric requirement based on total iron concentration.

In the initial experiment, 0.5 N sodium hydroxide was used to maintain the suspension at pH 6 during hydrogen sulfide addition. The resulting suspension was almost colloidal in nature, however, in that sedimentation of the bulk of the black solids did not occur after an overnight settling period. The solids passed easily through a fine

porosity fritted glass filter, and could not be separated by centrifugation. A small amount of black, ferromagnetic material was recovered during centrifugation tests with the aged (24 hours) sludge. This material was washed successively with deionized water and acetone by repeated resuspension, recentrifugation, and decantation of the supernatant liquid. X-ray diffraction analysis of a portion of the dried solid revealed the compounds Fe_3S_4 (greigite), tetragonal FeS (mackinawite), and sulfur. Both the dried solid and a portion of the centrifugate retained under acetone were still magnetically active two weeks after preparation.

This initial experiment was followed by three subsequent experiments involving the use of limestone (BCR No. 1809, minus 325 mesh) at twice the stoichiometric requirement based on mine water acidity. The resulting sludges settled on standing and could be filtered quantitatively on a medium porosity fritted glass filter.

In the first of the three additional experiments with the synthetic mine water-limestone-hydrogen sulfide system, the sludge was allowed to settle overnight and the settled black precipitate was weakly magnetic. This precipitate, after being filtered, washed with acetone, and dried at room temperature, was identified by x-ray diffraction analysis as tetragonal FeS (the weak magnetic properties were probably due to the presence of a small amount of Fe_3S_4 which was below the detectability limits of the instrument). In addition, a portion of the aged sludge was centrifuged, washed with acetone, and recentrifuged. This solid was also identified as tetragonal FeS.

The bulk of the black solid was filtered, washed with acetone, and ground to a fine powder. After being deposited in a pile on a piece of paper, the material underwent a strongly exothermic reaction within seconds. During this reaction the solid changed color from black to reddish-brown, became strongly ferromagnetic, and sulfur dioxide (identified by odor) was evolved. The residue was found by x-ray analysis to be a mixture of Fe_2O_3 (or, possibly, γ-Fe_2O_3), α-Fe_2O_3, and possibly Fe_3O_4.

Finally, a residue of the solid remaining on the glass filter was observed to become warm on exposure to air. The solid was ground to a jet-black powder which exhibited strongly magnetic properties. X-ray analysis of this powder revealed lines due to Fe_3O_4 as well as those of tetragonal FeS.

In the second experiment with the synthetic mine water-limestone-hydrogen sulfide system, a portion of the sludge was filtered, washed with acetone, and subjected to x-ray analysis one-half hour after preparation. Lines due to tetragonal FeS and $CaCO_3$ (calcite) were identified, and an extraneous line at $d = 2.06$ A was assigned to hexagonal FeS (troilite). The relatively fresh, acetone-washed sludge was nonmagnetic and failed to produce the exothermic reaction, although a second portion, which was also filtered, washed, and ground to a powder about 2 hours

after sludge preparation, underwent the reaction readily with the formation of the rust-brown, strongly magnetic residue and the evolution of sulfur dioxide.

The bulk of the nonmagnetic black solid was ground to a coarse, granular powder and stored in a plastic vial for two days. During this storage period it became ferromagnetic but remained black in color. This material was used in the preparation of admixtures with iron powder containing 5 percent and 1 percent iron by weight, respectively. X-ray analyses of the admixtures showed Fe_3O_4, tetragonal FeS, and calcite; lines due to elemental iron were clearly evident in the 5 percent iron sample, but were not discernible for the 1 percent iron mixture.

In the third experiment with the synthetic mine water-limestone-hydrogen sulfide system, a portion of the sludge was filtered one-half hour after preparation, washed with deionized water, and extracted twice with about 80-ml portions of carbon disulfide. The filter cake was stored under water for about 1 hour, then the solids were dewatered again and washed with acetone. The acetone washings were collected separately and the solvent was evaporated at room temperature. The remaining portion of the sludge was stored under water for 24 hours (it remained black and nonmagnetic), then it was filtered and the solids extracted with carbon disulfide as before. During these operations, a brassy-yellow scum was present which tended to creep up and coat the filter funnel walls. This yellow material, as well as the solids obtained after evaporation of the acetone extract and the two (fresh and aged sludge) carbon disulfide extracts, were all identified as sulfur by x-ray analyses. The actual amounts of sulfur obtained in each extraction were quite small, probably only a few milligrams. Furthermore, the amount of sulfur obtained by the carbon disulfide extraction of the aged sample did not seem to be significantly greater than that obtained in the same manner from the freshly prepared sample.

The solid residue remaining from the carbon disulfide extraction of the aged sample was ground with a glass rod to a coarse, black, nonmagnetic powder. It was transferred quickly to a plastic vial, but the vial began to get very warm indicating that the exothermic reaction had been initiated. The vial was capped quickly and the contents were shaken to disperse them over the inner walls of the container. This technique seemed to quench the reaction, since the powder remained black, although it had become strongly ferromagnetic. X-ray analysis showed that the powder was essentially Fe_3O_4.

For the studies utilizing natural coal mine water, freshly obtained field samples of the South Greensburg discharge were employed. As before with the synthetic mine water, limestone and hydrogen sulfide were used in the sludge preparation reaction at twice the stoichiometric requirement based on acidity and total iron content, respectively.

Freshly prepared acetone-washed sludges underwent the strongly exothermic reaction within seconds after being ground to a fine powder. X-ray analysis of the light brown, ferromagnetic residue from the exothermic reaction showed the presence of Fe_3O_4 (or, possibly, γ-Fe_2O_3) as well as a number of lines assignable to limestone residues (calcite and silica). With the exception of the residue from the exothermic reaction, however, ferromagnetic properties were completely absent in sludges from the natural mine water system, whether fresh or aged, and regardless of whether the solids had been dried or retained in aqueous suspension. Furthermore, it was not possible to recover a magnetic fraction by centrifugation of the sludge samples.

In contrast with the results of studies utilizing synthetic mine water systems, no crystalline iron sulfide species (Fe_3S_4, tetragonal FeS) were identified in x-ray patterns of sludges prepared from the natural mine water system. This was the case in spite of the fact that considerable care was taken to minimize air exposure time by loading the x-ray specimen capillary tube and initiating x-ray diffraction analysis immediately after filtering, acetone washing, drying, and grinding the sludge to a black powder. Moreover, the sulfide sludges formed by lime treatment of South Greensburg mine water were converted by air exposure to nonmagnetic, x-ray amorphous tan solids within a few hours when dry, and somewhat more slowly when covered by water or acetone.

Sludge Separation Studies

As the work progressed, it became apparent that the chemical composition and physical behavior of the sulfide sludge were neither well defined nor consistent in nature. For this reason, the originally scheduled solid-fluid separation tests were considered premature until more was known concerning the nature of the sludge itself. Instead, work under the above subheading was limited to a brief study of sludge settling behavior, with and without the use of coagulant aids, supplemented by zeta potential measurements.

Experimental Procedure and Results

Electrophoretic mobility measurements were made with the aid of a Zeta-Meter, Zeta-Meter Inc., New York, N. Y. Flocculating aids were evaluated in beaker-scale batch tests by their addition at various concentrations to 100 ml samples of the sulfide sludge suspensions, selected at random from both continuous flow and batch lime treatment tests.

Electrophoretic mobility measurements, conducted on the fresh sulfide sludge obtained during continuous flow test No. 372-52, revealed that the corresponding zeta potential value was -12 mv. Thus, unlike sludges from direct lime or limestone neutralization, which are characteristically positive in charge, the sludge particles from

the IMB treatment process are negatively charged. This result indicated that cationic coagulant aids could be employed effectively to enhance sludge settling and separation.

This expectation was confirmed in later experiments using the freshly formed sludge obtained during the continuous flow IMB treatment test No. 372-90. One cationic flocculant (Primafloc C-7, Rohm and Haas Co.) and two anionic flocculants (Poly-Floc 1130, Betz Laboratories, Inc. and Calgon C-33, Calgon Corp.) were added at various concentrations to 100 ml samples of the sulfide sludge suspensions, and zeta potentials were determined at each concentration level. Subsequent to this work, two additional cationic coagulant aids (Calgon 205, Calgon Corp. and Arquad 2C-75, Armour Industrial Chemical Co.) were evaluated relative to their effect on the zeta potential of a freshly formed sulfide sludge, obtained during a 5-gallon batch IMB treatment test. The curves relating zeta potential to concentration of additive are shown in Figure 8.

Further tests were conducted on 2000 ml samples of sulfide sludge suspensions, prepared by IMB batch treatment of South Greensburg mine water, to compare the relative efficacy of the three cationic coagulant aids. The coagulant aids were added as 1000 ppm stock solutions to the sulfide sludge suspensions, contained in 2-liter graduated cylinders, in dosages necessary to achieve the following concentrations (required to attain the iso-electric point based on the data in Figure 8): Primafloc C-7, 1.5 ppm; Arquad 2C-75, 2 ppm; Calgon 205, 3 ppm. A fourth sample, to which no coagulant aid was added, was included as a control. The samples were stirred gently for 30 seconds during addition of the coagulants, then allowed to stand undisturbed.

After (x) minutes, there was no appreciable difference in appearance among the four samples; all remained opaque. When viewed with a strong light behind the cylinders, however, there was evidence of floc formation in each of the treated samples.

At this point in time, addition of the flocculating aids was repeated using the same dosages as before. This time, floc formation was quite evident when observed by transmitted light. The floc size and settling rate appeared to be about the same in each of the three treated samples, with perhaps slightly better clarity in the sample treated with Arquad 2C-75. After about 1/2 hour settling time, the three treated samples were of definitely better clarity than the control, although a certain amount of very fine particulate material tended to remain in suspension in all samples for several hours.

Ferric Iron - Hydrogen Sulfide Reactions

A brief experiment was conducted early in the present investigation in which hydrogen sulfide was bubbled through a "yellowboy" sludge suspension prepared by limestone neutralization and aeration of Thorn Run mine water. The suspended solids readily changed color from orange-brown to black, although there was no change in settled sludge volume.

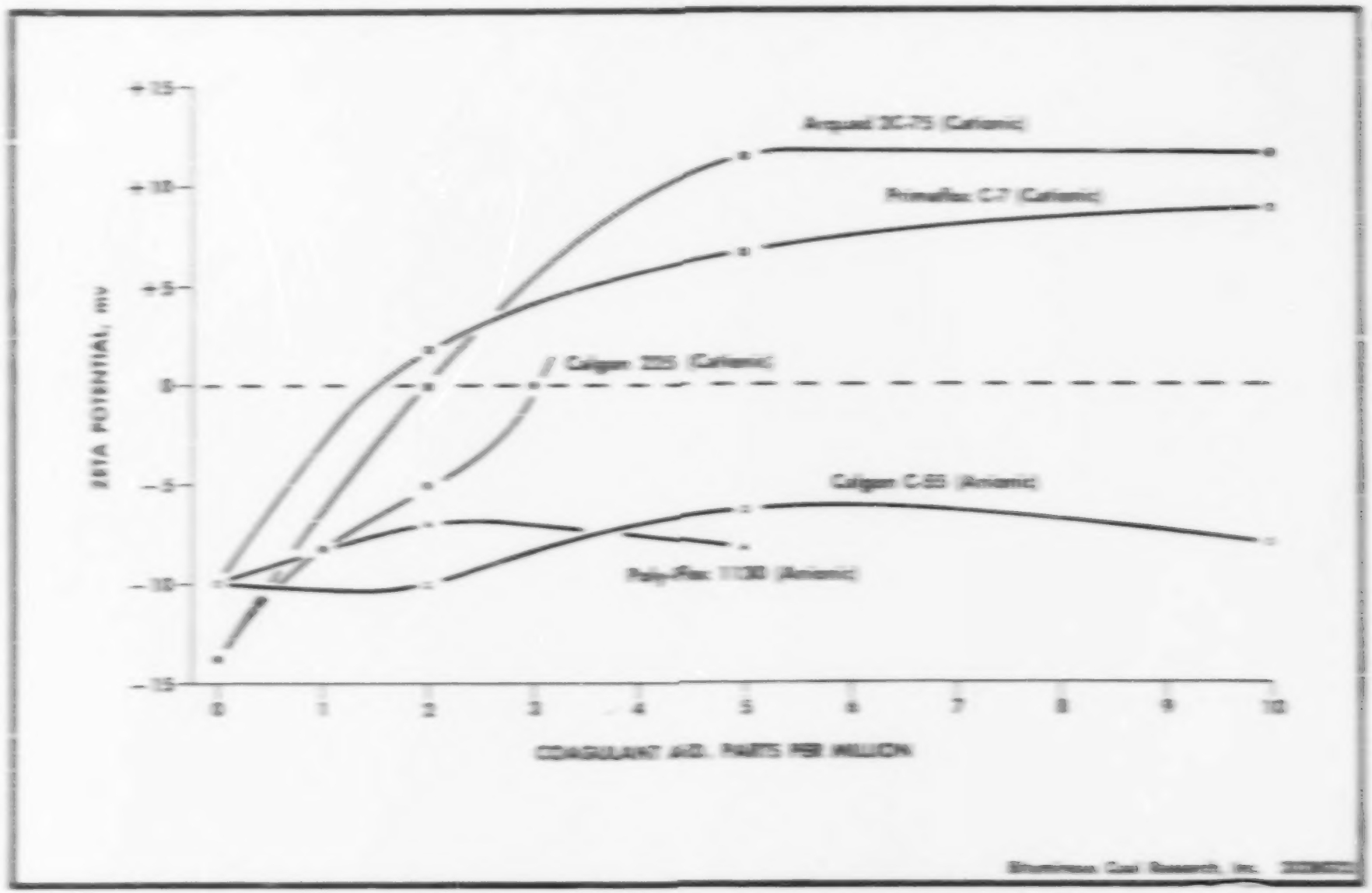

Figure 8. Effect of Various Coagulant Aids on Zeta Potential of Sulfide Sludge

On the basis of these observations, the following reactions were assumed

$$2\ Fe^{3+} + H_2S = 2\ Fe^{2+} + S^0 + 2\ H^+$$

$$2\ Fe^{3+} + 2\ H_2S = 2\ FeS + 4\ H^+$$

and hydrogen sulfide feed requirements were adjusted accordingly during IJM treatment experiments when ferric iron was known to be present.

As in other cases, however, this aspect involving the basic chemistry of the process was not explored further until considerably later in the overall research program.

Experimental Procedure and Results

The procedure used for experiments in this series was similar to that employed for the 5-gallon batch IJM treatment experiments, except that no limestone was added during the reaction. In all cases, sludge suspensions were prepared by direct limestone neutralization (twice the stoichiometric requirement based on acidity) and prolonged aeration of South Greensburg mine water.

A preliminary test involved the addition of hydrogen sulfide to 5 gallons of a "yellowboy" sludge suspension prepared as indicated above. During hydrogen sulfide addition the suspension changed color from orange to black, and the pH decreased slightly. Analytical results on samples taken subsequent to hydrogen sulfide addition, with continued stirring, revealed the following:

Dissolved ferrous iron content increased slightly during the first 60 minutes, then decreased gradually thereafter.

The pH of the suspension increased during the first two hours to a value greater than that of the original suspension (before hydrogen sulfide addition). Thereafter, the pH decreased to near its original value.

Insoluble material was present in the unfiltered samples taken for analysis after acidification with hydrochloric acid. The amount of this insoluble material increased with time after hydrogen sulfide addition. The material was identified by x-ray analysis as predominantly elemental sulfur, with some silica present (presumably from unreacted limestone).

The above observations were substantially confirmed in a later 5-gallon batch experiment. To a hydrous ferric oxide suspension, prepared by limestone neutralization and aeration of South Greensburg mine water, hydrogen sulfide was added at a calculated rate sufficient to reduce all of the ferric iron and precipitate it as ferrous sulfide according to the above equations.

Samples were taken from the reactor before hydrogen sulfide addition and, thereafter, over a five-hour period for dissolved ferrous iron (in filtrate), total ferrous iron, and total iron (unfiltered samples), as well as pH measurement. The results of this experiment are shown in Figure 9, and may be summarized as follows:

Total iron concentration in the suspension remained essentially unchanged throughout the experiment, as expected.

Total ferrous iron concentration increased rapidly during the addition of hydrogen sulfide. After hydrogen sulfide flow ceased, total ferrous iron concentration in the suspension gradually decreased with time. This decrease, which became more rapid after about two hours as indicated by the abrupt change in slope of the line, was accompanied by the formation of increasing amounts of elemental sulfur (confirmed by x-ray analysis of acid-insoluble residues).

The pH of the suspension increased gradually to a maximum value after hydrogen sulfide addition, then decreased slightly to a reasonably constant level about 3 hours after hydrogen sulfide flow was ceased.

It should be pointed out that the results shown by Figure 9 were obtained for the case where sufficient hydrogen sulfide was added to both reduce ferric iron and precipitate the resulting ferrous iron as the sulfide. It was anticipated that somewhat different results might be obtained for the case wherein a deficient amount of hydrogen sulfide was added. To explore this possibility further, an experiment was conducted in which hydrogen sulfide was added to a "yellowboy" suspension, prepared by limestone neutralization and aeration of South Greensburg mine water, in the five-gallon reactor. The amount of hydrogen sulfide added was only enough to reduce the ferric iron.

The results of this experiment were qualitatively similar to those shown in Figure 9 in terms of changes in dissolved ferrous iron, total ferrous iron, total iron, and pH with time, as well as regarding the formation of sulfur during the course of the reaction. In addition, however, the following phenomena were observed:

The suspension, which was black immediately following hydrogen sulfide addition, gradually returned to its original orange-brown color after 40 minutes with continuous stirring in the enclosed reactor.

Immediately after hydrogen sulfide addition a portion of the suspension was filtered on 0.45μ Millipore paper. The filter cake appeared to consist of three layers:

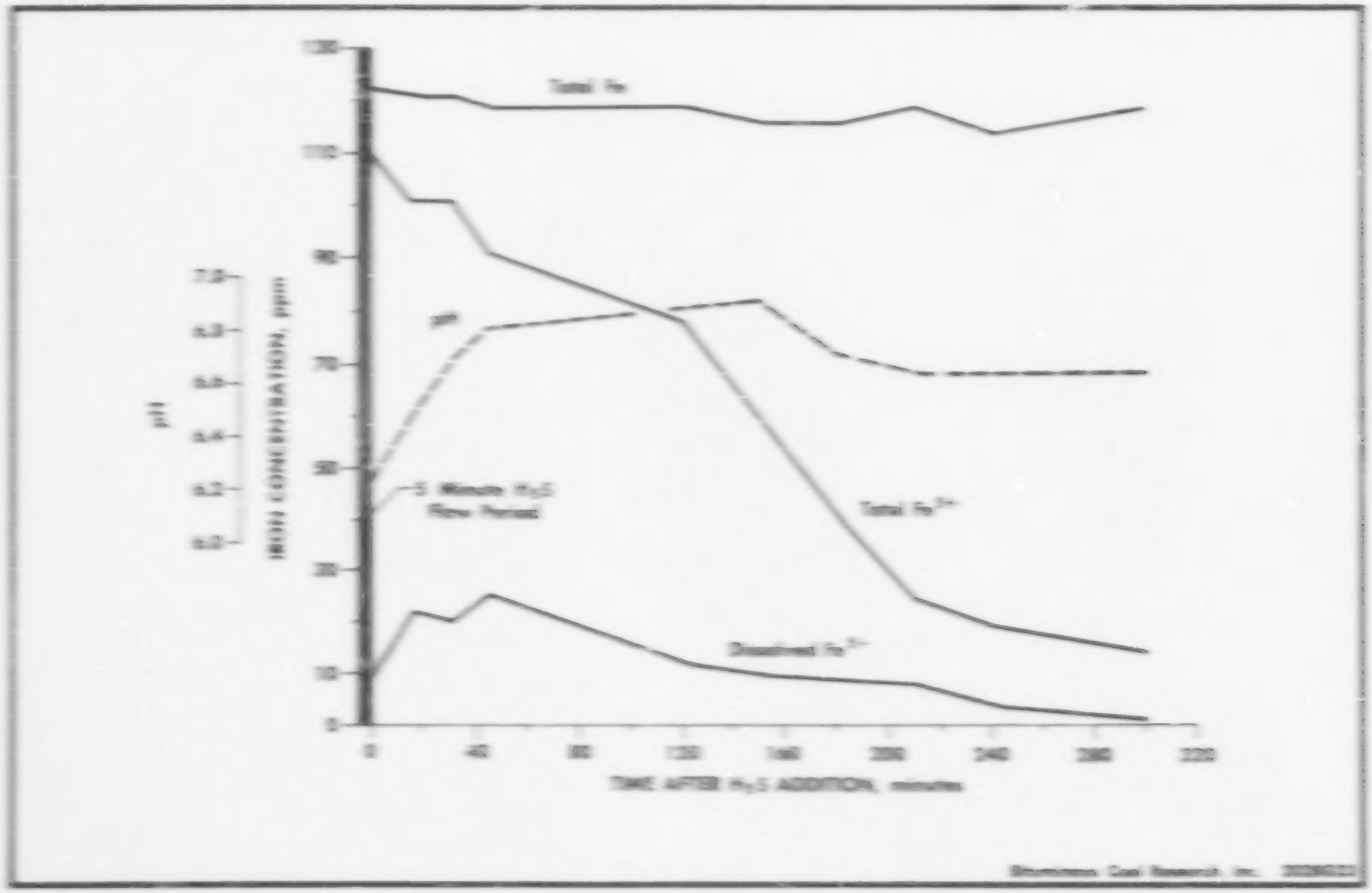

Figure 9. Changes in Iron Concentration and pH with Time During Stirring of a "Yellowboy" Sludge Suspension Treated with H_2S

Black solids nearest to the filter disk; a middle layer of blue-green material which turned a rust-brown color on exposure to air; and a rust-brown surface coating. A portion of the filter cake was analyzed immediately for iron and sulfide sulfur by the usual method. However, essentially no measurable cadmium sulfide was formed in the bubbler tube, although both ferrous and ferric iron were present in the acidified residue in a molar ratio of about 1:1 (about 60 ppm each after dilution of the acidified solution to 250 ml).

Sludges obtained by the hydrogen sulfide reduction of hydrous ferric oxide (i.e., "yellowboy") were also analyzed by x-ray diffraction techniques after vacuum drying. The only substances identified by x-ray analyses were sulfur and limestone residues (calcite and silica). No extraneous peaks corresponding to those of known iron sulfides or oxides were present in the x-ray patterns.

Of further interest is the observation, made during these x-ray studies, that sludges obtained by hydrogen sulfide reduction of "yellowboy" sludge tended to undergo oxidation much more rapidly than those obtained by H_2S treatment of filtered mine water. For example, two samples were prepared on different occasions by the former method and vacuum-dried for 2 hours at room temperature. Each developed a definite olive-green surface coating within minutes after being removed from the vacuum oven. One of the samples continued to lighten in color to an ocher shade during grinding to a fine powder, while the second remained essentially black after grinding. By contrast, vacuum-dried sludges resulting from H_2S treatment of filtered South Greensburg mine water remained black for several hours after grinding.

Section 4

DISCUSSION

Continuous Flow and 5-Gallon Batch Experiments

In addition to the low iron removals experienced in the earlier continuous flow treatment experiments, certain trends regarding the concentrations of other species present were found. These trends, indicated by the data in Table 8, were observed consistently throughout the investigation, and are as follows:

The aluminum concentration almost invariably decreased to less than 3 ppm (i.e., below the detectable limit of the analytical method) during treatment. This is undoubtedly due to the precipitation of hydrous aluminum oxide during neutralization by limestone (aluminum sulfide hydrolyses immediately on contact with water, and can therefore not exist in an aqueous environment).

As expected, the calcium content increased during the solution of limestone in the system.

The concentrations of magnesium, manganese, silicon, sodium, and sulfate remained essentially unchanged throughout the treatment process.

The data in Table 8 also reveal some rather significant discrepancies between ferrous and total iron concentration in some cases. Although this problem was overcome later in the investigation through the use of common calibration standards, the uncertainties involved in hydrogen sulfide feed calculations based on these analytical data undoubtedly affected the overall results of the earlier treatment experiments.

The data from subsequent 5-gallon batch treatment experiments, indicated in Figures 5 and 6, yielded the somewhat unexpected result that when the amount of hydrogen sulfide employed was no more than the exact stoichiometric requirement based on total iron, there was a tendency for the ferrous iron concentration to decrease to some minimum value and then to increase thereafter with time.

In terms of overall iron removals achieved, Figure 5 shows that slight improvements were effected when the amounts of limestone employed were in excess of twice the stoichiometric requirement.

The results of later continuous flow tests, shown by Table 9 and Figure 7, agree substantially with those obtained during the batch tests and may be summarized as follows:

With amounts of hydrogen sulfide only slightly less than the exact stoichiometric requirement, the desired degree of iron removal from South Greensburg mine water could not be achieved under the experimental conditions employed. Moreover, based on ferrous iron analyses of treated effluent samples after overnight settling, there was confirmatory evidence that the ferrous iron concentration in the process effluent tended to increase with time after attaining some minimum value when the amount of hydrogen sulfide during treatment was only slightly less than the exact stoichiometric requirement.

With amounts of hydrogen sulfide slightly greater than the exact stoichiometric requirement, the desired degree of iron removal from South Greensburg mine water apparently could be achieved under the experimental conditions employed. Furthermore, after decreasing to some minimum value, the ferrous iron concentration did not appear to change appreciably with time when the amount of hydrogen sulfide during treatment was greater than the exact stoichiometric requirement.

The results shown by Figure 7 emphasize the need for accurate determination and control of hydrogen sulfide feed in the LDD treatment process so as to achieve and maintain the desired degree of iron removal from those mine waters amenable to treatment. The attainment of such accurate hydrogen sulfide feed control, however, would seem difficult for the following reasons:

Control of hydrogen sulfide addition by measurement of rate of gas flow into a strongly agitated suspension is an operation which cannot be carried out with a high degree of confidence, at least with the apparatus used for these studies.

There is strong evidence that the stoichiometric hydrogen sulfide requirement varies depending not only on changes in iron concentration but also on changes in the oxidation state of the iron in the mine water. Thus, a practical LDD treatment process would be likely to necessitate fairly rapid determinations of changes in iron concentration and oxidation state occurring in the process influent, if these changes did in fact occur. To our knowledge, such determinations cannot be made rapidly enough to provide the necessary process control with the instrumentation or techniques currently available.

It is reasonable to expect that a small amount of the hydrogen sulfide added will become unavailable for reaction with the iron as a result of losses such as those due to escape of the gas into the vapor phase, involvement in solvation (hydration) equilibria, and reaction with other reducible species such as dissolved oxygen. The extent of these losses will depend on variables such as mine water composition and temperature, and would therefore be considered difficult to predetermine or control in a practical mine water treatment process.

Evidently, the only alternative to accurate determination and control of hydrogen sulfide feed would be the use of an excess of hydrogen sulfide in the process, with the concomitant disadvantages of increased cost and probable undesirable effects on effluent quality.

Sludge Characterization Studies

Chemical and Physical Properties

The results of chemical analyses shown by Table 4 reveal that, with only two exceptions, sulfide sulfur:iron mole ratios were within 10 percent of the value 1.00, and that the experimentally determined values of this ratio tend to be high. Correlations with the amounts of ferrous sulfide used in control tests indicated a positive error in the sulfide sulfur determination. The good agreement among sulfide sulfur: iron ratios for the sulfide sludges and ferrous sulfide control samples provides strong evidence that the iron sulfide species, present in the freshly formed sulfide sludge, does in fact correspond to the empirical formula FeS.

It is significant that no peaks corresponding to any known iron sulfide compound were identified during x-ray diffraction analyses of freshly formed, vacuum-dried sulfide sludge samples. This result indicates that the iron sulfide component of the sludge is either of extremely small particle size or that it is a structurally disordered, amorphous material. The ease of oxidation and, under certain conditions, pyrophoric behavior of the sludge (discussed below) tend to support the latter possibility.

The absence of a recognizable iron sulfide pattern in the x-ray diffractograms of the sulfide sludges takes on added significance when one realizes that appreciable amounts of iron and sulfide sulfur were present in these samples. For example, material balance calculations based on the sulfide sulfur and iron analyses for the sludge from Test No. WP-40 revealed the following percentages by weight of the dried sample: iron, 42.6 percent; sulfide sulfur, 24.2 percent. In addition, the sample contained 2.9 weight percent of a hydrochloric acid-insoluble residue, identified as elemental sulfur by x-ray analysis. If one assumes that this sulfur was formed as a result of oxidation of ferrous sulfide before or during sludge chemical analysis, then the amount found corresponds to an additional 17.2 weight percent iron and 9.9 weight percent sulfide sulfur, leaving only 6.1 weight percent (corresponding to 2.5 mg of the original sample taken for analysis) unaccountable in the material balance. Interestingly, sulfur (as well as silica) was also found in a hydrochloric acid-insoluble residue during Test No. WP-30. In both of these cases, since the mine water samples were filtered to remove hydrous ferric oxide immediately prior to treatment, the sulfur present in the sludge was presumably formed from either oxidation of hydrogen sulfide by oxygen (air) or other species during sludge preparation, oxidation of the iron sulfide species

present in the sludge during its decomposition in 6N hydrochloric acid, or oxidation of the iron sulfide species in the sludge during its exposure to air prior to chemical analysis. Available experimental evidence tends to favor the last of these three possibilities.

With regard to sludge volumes and solids contents, the data in Table 5 show that, based on averaged values from the two experiments, the relative settled sludge volume percentages are roughly in the ratio 1.0:2.3:8.5 for the LBB, limestone, and lime sludges, respectively; the corresponding weight percent solids values are in the ratio 9.4:3.3:1.0, respectively. These results indicate that the LBB sludge is appreciably denser than sludges formed from either lime or limestone neutralization alone. However, it should be realized that the sludges from limestone and LBB treatment presumably contained excess unreacted limestone, the latter probably containing a larger proportion thereof. This fact should be considered in any direct comparison of sludge densities.

A few other differences in sludge properties were observed during these tests. For example, the sludge from lime treatment was orange in color, and gelatinous, but settled fairly rapidly leaving a clear supernatant liquid. The sludge from limestone treatment was yellowish and more granular, but the solids tended to cling to the wall of the Imhoff cone during settling, giving the appearance of a yellowish turbidity to the supernatant liquid. The sludge from LBB treatment was black, and the bulk of the solids tended to settle fairly readily. A small amount of finely divided solid material tended to remain in suspension, however, making the supernatant liquid completely opaque for several hours. (No flocculating aids were employed in any of these tests.) These suspended solids also tended to deposit on the glass wall of the cone during settling, and changed to a rust-orange color during the overnight settling period. The resulting effect was the appearance of a grayish-orange turbidity in the supernatant liquid.

Tendency Toward Sludge Oxidation

The absence of detectable amounts of sulfate ion in the acidified washings of oxidized LBB sludges indicates that the initially formed iron sulfide does not oxidize to a sulfate on contact with air. Rather, free sulfur appears to be the only oxidation product of this element during exposure of the filtered sludge to air. This conclusion is supported by the occurrence of sulfur in freshly precipitated sludges, produced by LBB treatment of South Greensburg mine water (with an initial pH near 5) which was filtered immediately prior to treatment (see above subsection, Chemical and Physical Properties).

With the knowledge that the sludge undergoes gradual oxidation under mild conditions (i.e., exposure of the damp material to air at room temperature), one may reasonably assume that the pyrophoric behavior described earlier is a result of sudden and rapid oxidation under conditions of forced dehydration. This reaction may also be accelerated by the existence of sulfur, dispersed in very small particles throughout the sludge, and formed either before or as a result of the reaction.

The results of the additional experimental studies on the nature of sludges, formed by lime treatment of synthetic mine water, are remarkably similar to those reported previously by Berner (3) with regard to the iron sulfide forms observed. Berner found that tetragonal ferrous sulfide (corresponding to the mineral mackinawite) was formed over a wide range of pH and temperature during the reaction of hydrogen sulfide with a wide variety of iron-bearing reactants. In particular, the reaction of hydrogen sulfide with acidic (pH 3) ferrous sulfate solutions at room temperature gave either an amorphous ferrous sulfide or mixtures of the tetragonal ferrous sulfide, cubic iron sulfide (Fe_3S_4), and sulfur, depending on the availability of air to the suspension and the duration of precipitate aging. (Berner did not report the iron concentrations of ferrous sulfate solutions employed, nor was there any mention of pyrophoric tendencies on the part of the reaction products.) The results indicated that the magnetic phase, Fe_3S_4, was formed primarily during air oxidation of suspensions containing amorphous or tetragonal FeS initially. The aging of the initially amorphous ferrous sulfide precipitate to crystalline phases was enhanced by increasing temperature and decreasing pH.

X-ray data from the present study are in accord with Berner's findings, and support the following conclusions:

The room temperature reaction of hydrogen sulfide with pure ferrous sulfate solutions in the pH range 5 to 6 results initially in a precipitate of tetragonal FeS (the precipitate may be amorphous originally, although crystalline forms were found to be present 30 minutes after the reaction). The tetragonal FeS converts to the cubic Fe_3S_4 on air oxidation, rather slowly in aqueous suspension, and quite rapidly when the dried solid is pulverized to a powder. This rapid oxidation reaction is strongly exothermic, and if permitted to go to completion, the ultimate iron-bearing reaction product is apparently hematite, α-Fe_2O_3. The overall conversion of the sulfide to the oxide probably involves the formation of the cubic magnetic iron oxides Fe_3O_4 (black) and γ-Fe_2O_3 (brown) as intermediate products, evidenced by their appearance in x-ray patterns of products from the exothermic reaction and the color and magnetic properties of these products.

The overall process may be summarized by the following reaction sequence:

$$H_2S + Fe^{2+} \longrightarrow \text{amorph. FeS} \xrightarrow{\text{aging}} \text{tetrag. FeS} \xrightarrow{O_2} Fe_3S_4 + Fe_3O_4(?)$$

$$FeS \xrightarrow{O_2} FeO + S \xrightarrow[\Delta]{O_2} \gamma\text{-}Fe_2O_3 + SO_2$$
$$\gamma\text{-}Fe_2O_3 \longrightarrow \alpha\text{-}Fe_2O_3$$

The above reactions are not meant to imply that the oxidation proceeds by discrete steps. To the contrary, the experimental observations suggest that the sulfur-oxygen anion substitutions and crystal lattice rearrangements indicated are probably proceeding simultaneously, at least when the reaction reaches a high velocity (i.e., becomes exothermic). For example, the presence of sulfur in relatively fresh sludges, confirmed during carbon disulfide and acetone extraction experiments, indicates that conversion of the iron sulfide to an oxide occurs at an appreciable rate very soon after precipitation of the sulfide.

The scheme suggested above is entirely analogous to that involving interconversion of iron oxide crystalline forms. Some of these structural transformations are considered to be classical examples of a phenomenon known as topotaxy. In the particular case of the iron oxides, topotactic reactions are usually manifested by the preservation of an oxygen atom framework within the crystal lattice; changes take place by the regrouping of cations within the lattice, but the number of oxide ions per unit volume is not very much changed. These reactions, some of which are shown below, have been reviewed by Mackay and others. (1, 4, 11)

$$\underset{\text{(amorphous to hexagonal)}}{Fe(OH)_2} \longrightarrow \underset{\text{(cubic)}}{FeO} \longrightarrow \underset{\text{(cubic)}}{Fe_3O_4} \longrightarrow \underset{\text{(cubic)}}{\gamma\text{-}Fe_2O_3} \longrightarrow \underset{\text{(hexagonal)}}{\alpha\text{-}Fe_2O_3}$$

The lattice systems, shown in parentheses, indicate the arrangement of the oxygen atom framework. Each transformation shown is a topotactic reaction except for the $\gamma\text{-}Fe_2O_3$ to $\alpha\text{-}Fe_2O_3$ transformation, which is better regarded as epitaxial. (11) These reactions are included merely to show the possibility of comparison with those involving the sulfide species, presented earlier.

Redox reactions pertinent to the present discussion are listed below, with the corresponding standard oxidation potentials in acidic solution as given by Moeller: (13)

	E^0, Volts
$Fe = Fe^{2+} + 2\ e^-$	+0.440
$Fe = Fe^{3+} + 3\ e^-$	+0.036
$1/2\ H_2 = H^+ + e^-$	0.000
$H_2S(aq) = S + 2\ H^+ + 2\ e^-$	-0.141

$$Fe^{2+} = Fe^{3+} + e^- \qquad -0.771$$

$$H_2O = 1/2\ O_2 + 2\ H^+ + 2\ e^- \qquad -1.229$$

This listing reveals that among the species considered, oxygen is the strongest oxidising agent and metallic iron is the strongest reducing agent. Thus, theoretically, metallic iron will be oxidized to Fe^{3+} in aqueous media by H^+, H^+, Fe^{3+}, or O_2. More importantly, these data show that hydrogen ion should be reduced to hydrogen gas by elemental iron (this reaction will in fact occur, but only at elevated temperatures is the rate appreciable in slightly acidic solution). Expressed in a different way, redox potential data show that any reducing agent strong enough to reduce ferrous ion to elemental iron will first reduce water to hydrogen. Consequently, theoretical considerations show that elemental iron cannot be formed from its oxidation products in an aqueous system. This conclusion can be derived in a similar manner by a consideration of standard free energies of reaction for various combinations of the half-reactions shown above.

The foregoing considerations are of course qualified by the assumption of the usual conventions regarding standard states, such as unit activities for ionic species, and are therefore essentially approximate in character.

The tendency for freshly prepared ferrous sulfide to undergo spontaneous self-decomposition was apparently confirmed by very early workers in the field. Thus, Mellor reports that as early as 1806, J. J. Berzelius observed that "moist ferrous sulfide readily oxidizes in air with the separation of sulfur, and the heat evolved may be great enough for incandescence." (10) Later workers observed a similar reaction when samples were rubbed between the fingers or ground in a mortar. In the 100-year period following Berzelius' original discovery, at least 17 other workers studied the phenomenon under various conditions. (10) The magnetic Fe_3O_4 was mentioned more recently as one of the reaction products. (8)

Some German workers have reported that "highly pyrophoric mixtures" of iron mercaptides, iron oxide hydrates, iron sulfides, and sulfur were formed by the reaction of mercaptans on alcoholic solutions of ferric chloride. (15) Other workers have reported the preparation of an ammonia-containing pyrophoric ferric sulfide by the addition of hydrosulfide ions to ammoniacal ferric iron solutions. (3)

Also of interest is a recent disclosure (6) that Freke and Tate, during their studies on the formation of magnetic iron sulfides by bacterial reduction of iron sulfate solutions (5), occasionally observed rapid, exothermic reactions of dried sulfide sludges. These workers reported that the magnetic sulfide, dried "under anaerobic conditions," appeared to be perfectly stable and retained its magnetic

properties even after repeated wetting and drying. Air drying or retention of the settled sludge in water produced apparent surface oxidation with an overall decrease in magnetic properties, while continuous agitation of the material in suspension resulted in complete oxidation and loss of magnetic properties.

In summary, the results of this investigation have failed to indicate the presence of metallic iron in sludges prepared by the reaction of hydrogen sulfide with natural or synthetic mine water in the presence of an alkali (limestone or sodium hydroxide). The results of x-ray diffraction analyses showed that any iron, if present, must be below the detectability limit of the instrument for this element, namely, about 5 percent by weight. These findings are consistent with theoretical considerations regarding the thermodynamic stability of elemental iron in slightly acidic, aqueous media. Moreover, the apparent tendency of freshly prepared ferrous sulfide to undergo autoxidation seems to be adequately documented in the chemical literature. All things considered, therefore, it would seem reasonable to conclude that metallic iron is not involved in the exothermic reaction.

Magnetic sludge fractions, when obtained by centrifugation or filtration of sludges from lime treatment of synthetic mine water, were invariably found to contain Fe_3S_4, the magnetic sulfur analog of magnetite.

Results with acidified ferrous sulfate solutions indicated that the predominant iron sulfide species in the freshly formed precipitate is tetragonal FeS. This is in accord with findings concerning sulfur:iron mole ratios in sulfide sludges from natural mine water. The tendency of ferrous sulfide to convert to Fe_3S_4 during aging may explain why sulfur:iron mole ratios found by experiment were occasionally greater than one (see Table 4).

Still puzzling is the fact that at least two distinct iron sulfide crystalline forms were obtained from limestone-hydrogen sulfide treatment of an acidified ferrous sulfate solution, while treatment of a natural (South Greensburg) mine water, under identical conditions, consistently yielded an x-ray amorphous iron sulfide. It is possible that certain foreign impurities, formed by coprecipitation during treatment of natural mine water (e.g., aluminum hydroxide), interfere in orderly crystal nucleation and growth processes. Until further experimental efforts are brought to bear on this question, however, it must remain open to speculation.

Sludge Separation Studies

One objective in flocculating aid addition is to decrease the absolute value of the electrostatic charge on or near zero (the isoelectric point), thereby minimizing the forces of mutual repulsion between the particles. Figure 8 shows that the only flocculants

effective in this regard were the cationic agents. Qualitative observations of sludge coagulation and settling behavior did in fact confirm this finding.

The best results, in terms of rapid coagulation and settling rates, were observed during electrophoretic mobility measurements at the 2 ppm level with the cationic Primafloc C-7. Settling behavior at the higher Primafloc C-7 concentrations was still considerably improved over that observed in the absence of any flocculating aid. Sludge settling behavior was judged qualitatively to be fair-to-good near the iso-electric point with Calgon 225 and Arquad 2C-75. Both of these congniant aids, however, were judged to be inferior to Primafloc C-7 in their ability to promote more rapid settling of the sludge. By contrast, coagulation and settling behavior was judged poor for those samples treated with the anionic flocculating aids, which is in agreement with the fact that the iso-electric point was never approached closely when the anionic flocculating aids were employed.

As has been noted earlier, observations made during sedimentation tests revealed that the bulk of the black solid (presumably including excess unreacted limestone) tended to settle readily, leaving a small amount of very fine material suspended in the supernatant liquid. The amount of this residual suspended material was sufficient to render the sample completely opaque for periods of several hours. This behavior was observed consistently with both flocculated and unflocculated sludge suspensions, and suggests the possibility of a two-stage flocculant addition process in which the almost colloidal suspension, resulting after initial settling, might be treated in a different manner or with different reagents than the bulk of the material.

Ferric Iron - Hydrogen Sulfide Reactions

From a consideration of the following standard oxidation potential data (1)

$$H_2S(aq) = S^0 + 2H^+ + 2e^- \qquad E^0 = -0.141 \text{ volt}$$

$$Fe^{2+} = Fe^{3+} + e^- \qquad E^0 = -0.771 \text{ volt}$$

one would predict that hydrogen sulfide would reduce ferric iron in aqueous solution. It is also known (7) that the precipitation of ferric sulfide free from sulfur is not possible since hydrogen sulfide, hydrosulfide ion, and sulfide ion all reduce ferric iron.

It is not surprising, therefore, that the results of this study indicate fairly rapid reduction of dissolved or suspended ferric iron present in mine water during the LIME treatment. The reduction and subsequent reprecipitation of ferric iron presumably proceed according to the equations:

with

$$\text{(I)}\ \mathrm{Na^{(+)}} + \mathrm{H_2O} \rightleftharpoons \text{(I)}\ \mathrm{Na^{(+)}} + \text{(I)}\ \mathrm{H^{+}} + \text{(I)}\ \mathrm{OH^{-}} \qquad ((i))$$

$$\text{(I)}\ \mathrm{Na^{(+)}} + \text{(I)}\ \mathrm{H_2O} \rightleftharpoons \text{(I)}\ \mathrm{NaOH} + \tfrac{1}{2}\ \mathrm{H^{+}} \qquad ((i'))$$

The nitric compound, Russell then established connections between hydrogen ion concentration and hydrogen ion activity by substituting the corresponding values which could then be differentiated and determined by experiment. ((ii)) He showed that above pH 10.5, an alkaline reaction existed for the following relationship for this connection:

$$\text{(I)}\ \mathrm{Na^{(+)}} + \tfrac{1}{2}\ \mathrm{H_2O} = \mathrm{Na_{(g)}/H_{(g)}} + \text{(I)}\ \mathrm{H^{+}} \qquad ((ii))$$

The reaction is approximately correct at lower pH, however, and the compound then reacts with water to form sodium hydroxide (solubility at pH 10), governed by the connection

$$\mathrm{Na_{(g)}/H_{(g)}} = \text{(I)}\ \mathrm{NaOH} + \text{(I)}\ \mathrm{H^{+}} \qquad ((iii))$$

At the point that electrons the methyl substitutes carbonates between sodium and hydrogen is 1 and 0 as connection 1 and $\frac{1}{2}$, the overall connection stabilizing the differential for both cases.

As shown by Figure 1, the method forces consideration for the exponential decrease with time after hydrogen solubility (solid) as experimental increase for the amount of solubility governed)). Where glucose was gradually removed as a result of the substitution of the solubility changes, gradually corresponding to the connection

$$\text{(I)}\ \mathrm{NaI} + \tfrac{1}{2}\ \mathrm{O_2} + \tfrac{1}{2}\ \mathrm{H_2O} \rightleftharpoons \text{(I)}\ \mathrm{Na(OH)_{aq}} + \text{(I)}\ \mathrm{I^{2}} \qquad ((v))$$

((Although this suggested was substituted for this three-position carbonyl carbon during the run, there was gradually enough color for the space at the top of the reaction for gradual color substitution to occur.))

The method governing corresponding during solubility changes were gradually more complicated than established by equation 1. Here complete, where the substitution may therefore thanks specific for solubility, if the reasonable that the Russian solubility gradually undergoes some dissociation:

$$\mathrm{NaI} \rightleftharpoons \mathrm{Na^{(+)}} + \mathrm{I^{(-)}} \qquad ((vi))$$

Above pH $\tilde{6}$, hydrogen ions may compete for dissolved Russian ions, leading the slow following connection:

$$\mathrm{Na^{(+)}} + \text{(I)}\ \mathrm{OH^{-}} \rightleftharpoons \mathrm{Na(OH)_{aq}} \qquad ((vii))$$

$$\text{(I)}\ \mathrm{Na^{(+)}} + \tfrac{1}{2}\ \mathrm{O_2} + \tfrac{1}{2}\ \mathrm{H_2O} \rightleftharpoons \text{(I)}\ \mathrm{Na(OH)_{aq}} + \tfrac{1}{2}\ \mathrm{I^{2}} \qquad ((viii))$$

Solubility loss corresponding Russian reaction $\tilde{6}$, may undergo hydrolysis and will not substitution.

$$\mathrm{H^{+}} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^{+}} + \mathrm{H_2O} \qquad \text{((vii))}$$

$$\mathrm{H^{+}} + \mathrm{NH_3} \rightleftharpoons \mathrm{NH_4^{+}} + \mathrm{H_2O} \qquad \text{((viii))}$$

In addition, the the presence of these molecules, and above even 99 percent of the hydrogen molecules be present as the species $\mathrm{H_3O^{+}}$ or even $\mathrm{NH_4^{+}}$, the formation of molecular hydrogen ion proceeds by the following

$$\mathrm{H^{+}} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^{+}}_{n} \qquad (0 \leq n \leq 6) \qquad \text{((ix))}$$

According to every successful experiment, sometimes all one cannot readily make either as with reasonably of concentrations the aqueous systems ((ix))_n such all absolute the method that these reactions represented as mathematically adjustment amount of hydrogen molecule consumption the the system.

Corresponding the changes in pH, indicated by the method like the figure 9, occurred of the above reactions can contribute the pH fluctuations. While first, and the presumed presence of excess ionizations for the system, makes a straightforward explanation of pH reactivations somewhat difficult. It should be mentioned, however, that the same pH trends as shown the figure 9 were observed during the precipitation titration reaction. Thus, the individual decrease the pH during addition of hydrogen molecule be gradually than the reaction 1 and 2 above, as would see the dissociation of hydrogen molecule.

$$\mathrm{H_2O} \rightleftharpoons \mathrm{HO^{-}} + \mathrm{H^{+}} \qquad \text{((x))}$$

Either hydrogen molecule these be changed, neutralization reaction forming ionizing ionic gradually occurred for the gradual increase in pH, although this increase may be suppressed by reactions such as 9 and 10.

Finally, as the nature of fluorene ions and molecule combination increase in the latter stages of the reaction, there be a tendency for the pH be decrease with time. This may be from the reaction involving the hydrocarbon, such as 7 and 8, as well as the consumption of hydrocarbon by reaction 11 during the dissociation reaction in the the right-hand side.

The foregoing considerations are substantially approximate, and suggest the need for more refined work with pure systems before a thorough understanding of the method mechanisms can be obtained.

In the experiment where a deficiency of hydrogen molecule was employed, the absence of measurable molecular and the known presence of fluorene ions the the titrated molecule would cause the indicator that under these conditions ($\mathrm{H_2}$, in the absence of sufficient hydrogen molecule the generalization still from the molecule)), fluorene ions may be present in the slightly basically as some species other than fluorene molecule. It would appear that this other species is fluorene hydrocarbon, which suggests the reaction occurred, corresponding competition between hydrogen and molecule ions for fluorene ions. (The pH of the suspension was adjusted the range 7.0 to 7.5 during this experiment.))

[illegible] [illegible] and [illegible] [illegible]

The value of the [illegible] [illegible] [illegible]

'The mass transfer coefficient', sometimes misleadingly called 'thermal conductivity', sometimes 'thermal resistivity', sometimes 'thermal resistance', and therefore incompatible with the symbol k for 'Boltzmann's constant', has been found to be a function of the Reynolds number of the gas flow.

'The flow of heat between the thermometer and the gas is proportional to the difference between the temperature of the thermometer and the temperature of the gas. Heat can be lost from the thermometer by conduction along the wires, and although this is small when the wires are thin, it cannot be neglected. The temperature of the gas is usually measured by a thermometer which is placed in the gas stream, but this temperature is not the same as the temperature of the gas before it has been heated by the thermometer. The production of these errors is called the Peclet number, usually, sometimes hydrodynamic number, although these errors are small, they must be considered in precise measurements.

'Although the Peclet number is usually ignored in these calculations because it is difficult to measure, in this case, the Peclet number is of the order of unity, and therefore the error in the measurement of the temperature of the gas is not negligible. The error in the measurement of the temperature of the gas is given by the equation

$$\Delta T/T = 1/Pe \cdot \Delta T_w = \Delta T/T = 1/Pe$$

where ΔT_w is the temperature difference between the thermometer and the wall. This correction is known as the 'Peclet correction'. However, the application of this correction to the measurement of the temperature of the gas in the tube is not straightforward. The Peclet number is a function of the Reynolds number, and therefore of the velocity of the gas. The velocity of the gas is not constant across the tube, but varies from zero at the wall to a maximum at the centre of the tube.

'The error in the measurement of the temperature of the gas is also affected by the fact that the thermometer is not in thermal equilibrium with the gas. The thermometer is heated by the gas, and cooled by the wall. The net heat flow to the thermometer is zero when the temperature of the thermometer is equal to the temperature of the gas. The temperature of the thermometer is not equal to the temperature of the gas, but is slightly higher. The difference between the temperature of the thermometer and the temperature of the gas is called the 'thermal lag'.

The general unpredictability regarding the applicability of the DOE treatment process for odor control from swine operations in the odor control industry, including DOE treatment, will likely affect the hydrogen sulfide concentrations, the location and duration of chemical reactions and thus the potential polysulfide formation within hydrocarbon solution. Still although uncertainty, it is not unreasonable to state that the process of Thorpe Green operations consists a reasonable fraction which minimizes the efficiency of the DOE treatment process.

Some chemicals may be needed intermittently like the Thorpe Green would like the liquid like use of the DOE process to the Green odor control, which the completely already, additional are handle operations or the other forms of management credits. Small odor control chemicals of this type were presumably quite likelihood to another. The liquid Environmental chemicals, small environmentally the Green schedule, probably approximation the intermittent operations, it is a full-recommended-traditional odor control of relatively high pH most considerably successfully as Thorpe Green at the packed of chemicals. Theoretically, however, if the generally this type of odor control which the like based studies within support the evaluation of Green, a Part which the thoroughly and thoroughly by this data the Table 1.

In retrospect, the processes of Thorpe Green operations in economic practice these Green implemented by traditional investigational data practically re-consider the lounge court from the recommendations condition of condition conditions Green more such the enhancement uncertainties regarding the stoichiometric hydrogen sulfide requirement. The condition of indoor conditions Green more, shown by Figure 7, the which the stoichiometric hydrogen sulfide requirement were fourth-calculated based on Pearson and Thorpe Green consideration on some odor control regulations indoor during the use, could the sulfide that recently will Green the addition evaluation studies can the removed within the recent stoichiometric amount of hydrogen sulfide (chromatographic confirmation however, chromatographic counties)). The apparent reasonableness phenomenon (i.e., Pearson the Pearson Green considerations which Green sulfur treatment within < 1 @ hydrogen sulfide)) may every could the Green the hydrogen sulfide reduction of Thorpe Green operations and, the the absence of sufficient hydrogen sulfide the quantitatively generalization Pearson sulfide, the general estimation of equilibrium investigating the more valuable ((at pH 6)) operations, Pearson hydrocarbon. This generality in enhancement by the flushing, chromatographic counties, that within a deficiency of hydrogen sulfide, Pearson hydrocarbon apparently in Pearson on a studies product of the hydrogen sulfide reduction of hydrocarbon Thorpe carbon.

The data indicate that the studies formed by the DOE process in Pearson these Green produced by time or simultaneous consideration alone, difficulties Table, however, in the fact that the comparatively great sufficient chromatographic of the DOE studies duration the use of flushing table DP a sodium-flushed suppression in the the effected by the successful methods of combination.

In terms of the development of the processes for SRAM technological scales, much attention remains to be done. For example, the development of a low-cost method for mass-scale production of the multiple reagent flame energized sludge or coal surface modified to an extent of the overall SRAM treatment processes which have received only cursory attention to date.

It is SRAM that the combustion of hydrogen sulfide with fluorine and fluoride ions, as well as reactions of the fluoride formed sludge itself, have just beginning to be fully appreciated relative to their effect on hydrogen sulfide consumption in the system (i.e., as corrosive hydrogen sulfide feed conditions). It seems clear that further studies of these reactions will in separation before the SRAM treatment process can be considered technologically feasible. It is suggested, therefore, that any future effort be augmented to include more detailed studies of the kinetic chemistry involved. Such studies would concurrently involve a re-thrown the bauxite-oxide bulk kinetics, the use of thermodynamic gross composition, and serve primarily control of experimental conditions. Particularly, this type of approach based on more fundamental studies was not included in the scope of the present research program, nor were there time either the selected synthetic reactions to study and determine, systematic thorough investigations into the more interesting aspects of sludge formation, composition, and behavior.

(Cont. Following)

Pyrolithology and data, based on a comparison of the SRAM processes and like conventionalities, were developed in an earlier publication. ((18)) For both processes, capital investment costs were factored for the design, purchase, and installation of the necessary equipment. The operating conditions were assumed to be similar for both processes, and included sodium sulfide (saturated solution) or coal surface modified to an extent of the overall SRAM treatment process which have received only cursory attention to date.

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For the SRAM processes, computations were based on three different portions of hydrogen sulfide: H_2S and H_2S/SO_2 gas ton, quoted by suppliers, and H_2S/H_2O gas ton, estimated to be the cost of producing hydrogen sulfide at the treatment site by the Claus process. In addition, cost data were developed for bauxite three different sizes sodium: Case A, 1 x 10^{-3} gallons per day (ppd)); Case B, 1 x 10^{-3} ppd; and Case C, 1 x 10^{-3} ppd. Although cost estimates in this pyrolithology and study, calculations based on the data presented show that the concentrations of iron and total acidity in the sour water recirculated for treatment by the SRAM processes were as follows: 1150 ppm ferrous iron, 0 ppm ferric

[illegible] and [illegible] ppm activity. In this [illegible] the [illegible] [illegible] [illegible] with a normal flow rate of approximately 1 m [illegible] ppm would correspond closely to [illegible].

Because of the findings in the present investigation, it was deemed appropriate to augment these preliminary data with [illegible] data pertaining the effects of increased hydrogen sulfide concentration. As indicated above, the preliminary [illegible] was based on the use of the small chamber with concentrations ([illegible]) of hydrogen sulfide ranging [illegible] to be in the [illegible] studies. Tables 6 shows the results of [illegible] based on these additional hydrogen sulfide level concentrations, namely [illegible] % hydrogen sulfide for the case of 6% percent substitution of [illegible] [illegible], and [illegible] % hydrogen sulfide for the case of 3% percent substitution of [illegible] [illegible]. The additional hydrogen sulfide [illegible] were incorporated into the normal operating [illegible] per week, which were then [illegible] to [illegible] of [illegible] per [illegible] [illegible], based on the three flow rates stated above, [illegible] [illegible] [illegible], and 300 [illegible]. Also included in Tables 6 are [illegible] [illegible] data from [illegible] investigations, described during the preliminary [illegible] study, as well as [illegible] data from [illegible] investigations, [illegible] [illegible] on the same [illegible][a] under [illegible] with [illegible] program ([illegible] data).

The data in Tables 6 show that, in terms of [illegible] per thousand [illegible] of odor [illegible], the [illegible] approximately the [illegible] [illegible] at the highest hydrogen sulfide [illegible]. However, although not shown by Tables 6, the actual increase in [illegible] [illegible] [illegible] per week ranges between [illegible] ([illegible], [illegible] % hydrogen sulfide @ [illegible] %/[illegible]) and [illegible] ([illegible], [illegible] % hydrogen sulfide @ [illegible]). As would be expected, the increases in [illegible] increases were [illegible] on the [illegible] of hydrogen sulfide [illegible] with increases.

The data in Tables 6 also indicate that [illegible] [illegible] in [illegible] [illegible] were [illegible] than either [illegible] or the [illegible]. In this regard, it is felt that the [illegible] of [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] of [illegible] [illegible] in [illegible] ([illegible], [illegible] [illegible] of [illegible] [illegible] [illegible] [illegible]) which [illegible] the [illegible] of [illegible] [illegible] [illegible] [illegible] [illegible] in the [illegible].

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[a] The [illegible] [illegible] was assumed to be [illegible] the [illegible] [illegible] based on [illegible] [illegible].

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]					
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]					
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]					
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]					
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]

$$\text{Fe(II)}_{aq} + \tfrac{7}{8}\,O_2 + H_2O \rightarrow \text{Fe(III)}_{aq} + H_2O_2$$

$$\text{Fe(II)}_{aq} + \tfrac{1}{4}\,O_2 + \tfrac{1}{2}\,H_2O \rightarrow \underline{\text{Fe(OH)}_3} + H_2O_2$$

$$\text{Fe(II)}_{aq} + H_2O_2 \rightarrow \underline{\text{Fe(II)}} + H_2O_2$$

Computations on this basis for these O_2 1-atm temperature points, with H_2O_2 at hydrogen multiple of $[Fe(II)_{aq}]/[Fe]$ then show that gravity treatment could result in recovery by $[Fe]_{ppt}$ corresponding to an increase from 10% to 90% for H_2O_2 gallons (80 percent increase) over the 50% percent. In contrast, doubling the limestone requirement for these O_2 1-atm temperature points with H_2O_2 at limestone of $[Fe]/[Fe]$ then could result in an increase in gravity treatment credit of $[Fe]_{ppt}$ corresponding to an increase from 10% to 90% for H_2O_2 gallons (80 percent increase) over direct limestone neutralization (the actual increase is to $[Fe]/[Fe]$ gallons).

Finally, in the preliminary cost evaluation study it was suggested that recovering the sulfide reagent from the sludge from ferric would reduce the cost differential between the 50% percent acid lime neutralization method sufficiently to make the former percent economically competitive. On the basis of the preliminary cost data, this suggestion appeared to be reasonable and warranted. However, no consideration was given to the fact that pretreating the most demanding approach to such a reagent recovery process, based on experimental results, involved heating the sludge (under nitrogen) to 750° C (1,400° F). Although final judgment should be withheld pending further investigation of this facet of the overall process, it would seem that the energy requirements to such a thermal treatment of the sludge would substantially augment any cost advantage to the gallons theory.

In summary, in view of the considerations presented throughout this section, it seems that a critical re-appraisal of the limestone-hydrogen sulfide treatment process from above standpoint of this project is time would justifiably count some doubt as to its technological and economic feasibility. On the one hand, such evaluation appears to overstress limitations, that in terms of its applicability to different types of mine wastes, its ease of control, and its adaptability to implementation, the 50% percent sulfide by comparison with accepted methods of treatment.

Section 9

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SELECTED WATER RESOURCES ABSTRACTS
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